Chemical Engineering Series

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CHEMICAL ENGINEERING SERIES

INDUSTRIAL STOICHIOMETRY

CHEMICAL CALCULATIONS OF MANUFACTURING PROCESSES

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CHEMICAL CALCULATIONS OF MANUFACTURING PROCESSES

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TO

WILLIAM H. WALKER

PIONEER IN CHEMICAL ENGINEERING WHOSE
TEACHING FURNISHED THE INSPIRATION FOR THIS BOOK.

PREFACE

Stoichiometric methods of computation are taught in every course in Quantitative Analysis, but frequently no analogous training accompanies the instruction in Industrial Chemistry. This is unfortunate, because the ability to interpret data quantitatively is of inestimable value in industrial work. In both laboratory and plant the same fundamental, natural laws apply, but in the two cases there are important variations of conditions that greatly influence the quantitative methods of using them, making the technique of industrial computations decidedly more involved and difficult to master than that of quantitative chemistry.

Little study is required to bring out some of the essential differences between laboratory and plant conditions. Thus, in analytical chemistry a quantity of the material to be investigated is taken, kept carefully isolated from its surroundings to prevent either loss or contamination, and put through a series of chemical transformations, conducted with little regard to expenditure of either time or money. These conditions are specifically chosen to eliminate all impurities and finally to convert the component which it is desired to evaluate into a chemically pure form in which its quantity can be measured either directly or indirectly, by weight or otherwise. It is rare indeed that industrial processes do not deviate from these conditions in one or more important respects. Thus, in the burning of coal, sulfur or pyrites, no one part of the material treated is isolated from the rest, but, when fed to the furnace, it mixes with material already there which is partially burnt, and, later, with fresh charge introduced at a subsequent time. Similarly, while it is desirable to have chemical conversion under industrial conditions as complete as practicable, it is almost never economically advisable to try to make reactions quantitative in the analytical sense, because the cost is greater than the advantage gained. Again, the reaction products instead of being isolated in the pure state, are frequently employed as they are, either directly or as starting

points for further reactions. It is obvious that such essential differences necessitate modified methods of stoichiometric interpretation.

In industry, two important methods of operation are the batch and the continuous types. Illustrations of the first are the conversion of pig iron into steel in the open hearth furnace or in the Bessemer converter, the decomposition of sodium nitrate with sulfuric acid, the graphitization of electrodes in the electric furnace, the sulfonation of benzol in an autoclave, etc. Illustrations of continuous processes are the operation of a contact sulfuric acid converter, the absorption of ammonia and light oil from coal gas, the calcining of cement rock in a rotary kiln, the formation of paper on the Fourdrinier, and the like. Intermediate between these stand semi-continuous processes, such as the operation of the ring furnace and the blast furnace, the extraction of such materials as tan bark and black ash by counter current lixiviation, the tube and tank cracking process for the production of gasoline, the glass tank furnace, and many others. In a given plant, operations belonging to various types may be tied in with one another. One of the important factors in industrial stoichiometry is the differentiation between these types of operation.

In a sense, batch operations differ in type from those of quantitative analysis only in the scale upon which they are conducted. Hence the computation methods of batch operation are identical in principle with those of quantitative analysis and, because of this fact, require but little emphasis here. Continuous and semi-continuous processes are less frequently met in the laboratory and the computation methods applicable to them are so seldom developed in the classroom that in the following pages they demand more complete treatment.

Adequate control of process and design of equipment involves consideration of three groups of factors, each separate from the others, yet all three intimately interrelated in determining final results. The first group comprises the quantity relationships included in the laws of stoichiometry in the narrower sense of that word, *i.e.*, the laws of the conservation of matter and of the elements, and the law of combining weights, but including also the law of the conservation of energy. The second group involves the equilibrium relationships of chemical reactions and the third the rate relationships. The second determines to what

extent it is possible to carry any given reaction under any given set of conditions and the third determines the production capacity of the equipment. In engineering work no one of the three can be ignored, but in a certain sense the first group are the basic, underlying relationships. It is with the first group alone that this book deals.

All quantitative work must be based upon adequate and dependable data. It frequently happens that quantities industrially important are not subject to direct measurement or can be determined directly only at great expense. It is, however, always true that certain data are readily and accurately determined. By the use of data of this sort, at times supplemented by auxiliary measurements so chosen that they can be made with a maximum of accuracy and at a minimum of expense, it is almost always possible to compute the quantities it is necessary to know. Furthermore, the computation methods can be free from assumptions, which are open to question. This habit of letting the head save the heels is an important asset in engineering work. Throughout this book especial emphasis is laid upon this phase of the problem. The reader will note that, in general, the data given are easily and accurately obtainable and are used to compute quantities industrially important which would be economically expensive to measure directly. In the preliminary presentation of topics, the illustrations are chosen, not from this point of view, but to familiarize the beginner with the concepts in the clearest possible way.

No accountant considers his work complete until his books are balanced, for, while balancing does not prove the figures correct, it offers an important check upon their dependability. It is surprising how seldom the engineer employs this principal of balance in checking the accuracy of his figures. Technical reports containing inconsistent data, the incompatibility of which was never recognized by the writer of the report, are too frequently encountered. One reason for this situation undoubtedly lies in the fact that the technique of cross-checking industrial chemical data is more involved than that of cost accounting. It is, however, no less important and has consequently been made one of the major points of emphasis in this book.

Because of the saving of time and of the fact that industrial computations so rarely justify higher precision, the slide rule

has been used almost exclusively. It is, however, important to recognize those cases in which greater precision is essential.

The teaching experience of the authors convinces them that one of the glaring weaknesses of the beginner is inability to think clearly and accurately in terms of arithmetic. As preliminary exercises to overcome this difficulty, problems of the type given at the end of Chapter I and in connection with Chapter IX will be found helpful. From this angle it is sometimes desirable to take up Chapter IX immediately after the Introduction, before going on with Chapter II and the rest of the book.

It is hoped this book will prove of real value, not only as a supplementary text in connection with classroom instruction in Industrial Chemistry, but also as an aid in the technique of computation to all those interested in the chemical phases of industry.

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Cambridge, Mass., and
Alfred, N. Y.
April, 1926.

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INDUSTRIAL STOICHIOMETRY

CHAPTER I

INTRODUCTION

Industrial stoichiometry is the application of the laws of the conservation of matter, of the elements and of energy, and of the chemical laws of combining weights, to the processes and operations of industrial chemistry. Because these laws are all of absolute validity,[1] conclusions correctly based upon them cannot be questioned, and this fact gives them their outstanding importance in industrial work. They are invaluable in determining quantitative interrelationships and the dependability of data. The purpose of this book is to develop the technique of using them most effectively under the conditions of industrial practice.

While the method of presentation employed in the following chapters involves mastering general principles by studying their applications in specific cases, it is none the less desirable to summarize in this chapter the fundamental concepts and certain basic data found useful in nearly all cases. This summary is a brief review of certain elementary principles of analytical and physical chemistry, indicating also the modifications in the method of using them in English units.

Molal Units.—As in analytical and physical chemistry, so in industrial stoichiometry, it is frequently advantageous to use the mol as the unit of quantity. Whereas, in scientific work the gram mol is employed almost exclusively (*i.e.*, a weight in grams equal to the molecular weight of the substance in question), in industrial work the pound mol, a weight in pounds

[1] The ordinary form of the law of conservation of the elements must, of course, be modified when dealing with radioactive elements, but even in this case the correction is usually negligible, except when dealing with such elements of relatively short life. Furthermore, when dealing with isotopes, the proper atomic weights must be used. Obviously, however, in the overwhelming majority of industrial problems no such qualifications come into consideration.

equal to the molecular weight of the material, is often more convenient. Where any doubt exists as to molecular weight, as, for example, with materials subject to partial dissociation or to polymerization or the like, the value of the molecular weight employed must be clearly indicated, corresponding to the value employed in writing the chemical equation. Frequently, the gram atom or pound atom is also used, and is sometimes loosely referred to as mol Since there are 454 grams per pound, it follows that a pound mol is 454 gram mols, but, as will appear later, this relationship is seldom used.

Gas Laws.—The behavior of the so-called "perfect gases" is indicated by the gas laws as represented by the equation, $pv = nRT$. In this equation p is the absolute pressure of the gas, v is its volume, n is the number of mols of the gas under consideration, R is the gas constant and T is the absolute temperature. Both pressure and volume can be in any units desired and the temperature on any scale, but the scale must start at the absolute zero. The quantity of the gas in mols can also be expressed in any units but only the gram mol, kilogram mol and pound mol are ordinarily employed. The gas constant, R, is the same for all gases but its numerical value depends on the units in which the other quantities in the equation are expressed. For pressures in atmospheres, volumes in liters, quantities in gram mols and temperature in degrees Centigrade absolute, the gas constant, R, is 0.08207. For pressures in lb. per sq. ft., volumes in cu. ft., quantities in lb. mols and temperatures on the absolute Fahrenheit scale, R equals 1543.

Since the absolute zero of temperature is approximately −273°C., *i.e.*, −460°F., these quantities must be added to temperatures on the Centigrade and Fahrenheit scales respectively to get absolute temperatures. Absolute temperatures on the Centigrade scale are frequently called degrees Kelvin (°K.) and on the Fahrenheit scale, degrees Rankine (°R.).[1]

The deviations from this equation of the so-called "permanent gases," *i.e.*, those whose critical temperatures are well below atmospheric temperature, are slight up to pressures of several atmospheres, and for most purposes usually negligible at 1 atm. or less, and at normal and higher temperatures. At pressures below atmospheric, the deviations of other gases and even of

[1] It should be kept in mind that while the melting point of ice is 0°C. (273°K.) it is 32°F. (492°R.).

saturated vapors seldom exceed 2 or 3%. Furthermore, the lower the pressure and the higher the temperature the less the deviations.

Another law applicable to all gas mixtures, the components of which follow the gas laws, is Dalton's law relative to the additivity of partial pressures. It is easily seen that in any mixture of gases following these laws, the volume per cent of any component is equal to the mol per cent of that component and is also equal to the partial pressure of that component expressed as a percentage of the total pressure. This may be written:

$$\text{volume per cent} = 100\,(\text{mol fraction}) = 100\,\frac{\text{partial pressure}}{\text{total pressure}}.$$

This rule is used in all volumetric gas analyses. Such analyses are always made at atmospheric pressure or below, and, in general, the partial pressures of the individual components are so low that the deviations from the gas laws are less than the manipulative errors of analysis. However, should conditions where this is not the case be encountered, analysis must be made by other methods or else the results corrected for the deviations. It is, however, perfectly allowable to make gas analyses at low pressures where the gas laws hold, and then to use the analytical results under higher pressures and lower temperatures where the deviations may be very large, since a change in temperature or pressure alone cannot possibly produce a change in the composition of a mixture as a whole.

Exactly as in the solution of problems in analytical and physical chemistry, it is frequently most convenient to use the gas laws in terms of the gram-molecular volume, 22.4 l., *i.e.*, the volume of 1 gram mol of any gas under standard conditions of temperature and pressure—so in industrial work, it is frequently desirable to use the pound-molecular volume, which is 359 cu. ft. under standard conditions of temperature and pressure, namely, the freezing point of water and 1 atm. Indeed, it is not infrequently convenient to define the molecular weight of a gas as the weight in pounds of 359 cu. ft. of the gas, measured at standard conditions. Variations in temperature and pressure are then readily allowed for by proportion.

Heat Quantities.—In the metric system, the unit of heat is the gram calorie (cal.), and in the English, the British thermal unit (B.t.u.) and the Centigrade heat unit (C.h.u.). The latter is

the heat necessary to raise 1 lb. of water 1°C., and since 1°C. = 1.8°F., 1 C.h.u. = 1.8 B.t.u. In almost all chemical work, the thing of interest is the ratio of the amount of heat to the amount of material under consideration, and a little study will make it clear that such a ratio in gram calories per gram is numerically identical with the same ratio in C.h.u. per pound. Thus, the statement that a certain liquid has a specific heat of 0.5 means that it requires 0.5 cal. to raise 1 g. of the liquid 1°C. Obviously, it also requires a numerically equal quantity of heat, 0.5 C.h.u., to raise 1 lb. of the liquid 1°C.

Heats of chemical reactions are almost always given on a molal basis, corresponding to the chemical equation as written in connection therewith. Thus, the equation,

$$CaO + CO_2 = CaCO_3 + 42{,}500 \text{ cal.},$$

means not only that 56 g. of CaO combine with 44 g. of CO_2 to form 100 g. of $CaCO_3$, but also that the combination of these quantities of reacting substances to form this amount of product evolves 42,500 cal. of heat, *i.e.*, sufficient to raise 42,500 g. of water 1°C. It should be obvious that if 56 lb. of CaO combine with 44 lb. of CO_2 to form 100 lb. of carbonate, the heat evolved will be sufficient to raise 42,500 lb. of water 1°C., *i.e.*, will be numerically equal to 42,500 C.h.u.

The molal heat capacity of a material is the amount of heat necessary to raise 1 mol of the substance 1° and is, therefore, its specific heat times its molecular weight. For certain groups of gases, the molal heat capacities of all members of the group are the same, or substantially so. Thus, for the monatomic, permanent gases, the $MC_p = 5.0$, substantially independent of the temperature. For the permanent diatomic gases, $MC_p = 6.5 + 0.001T$, where T is in degrees Kelvin (degrees Centigrade absolute). For gases of more complicated structure, the formulas are more involved.[1] In stoichiometric computations, one is almost always interested not so much in the heat capacity as in the total heat quantity corresponding to a given change of temperature. Because the computation of such quantities is somewhat involved, it is more convenient to represent them by a diagram (see Figs. 1 and 2). While these figures give the total sensible heat per mol of gas above the freezing point of water as a base line, the

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **34**, 1128 (1912).

heat quantity corresponding to any given change in temperature is equal to the difference in the corresponding ordinates.[1]

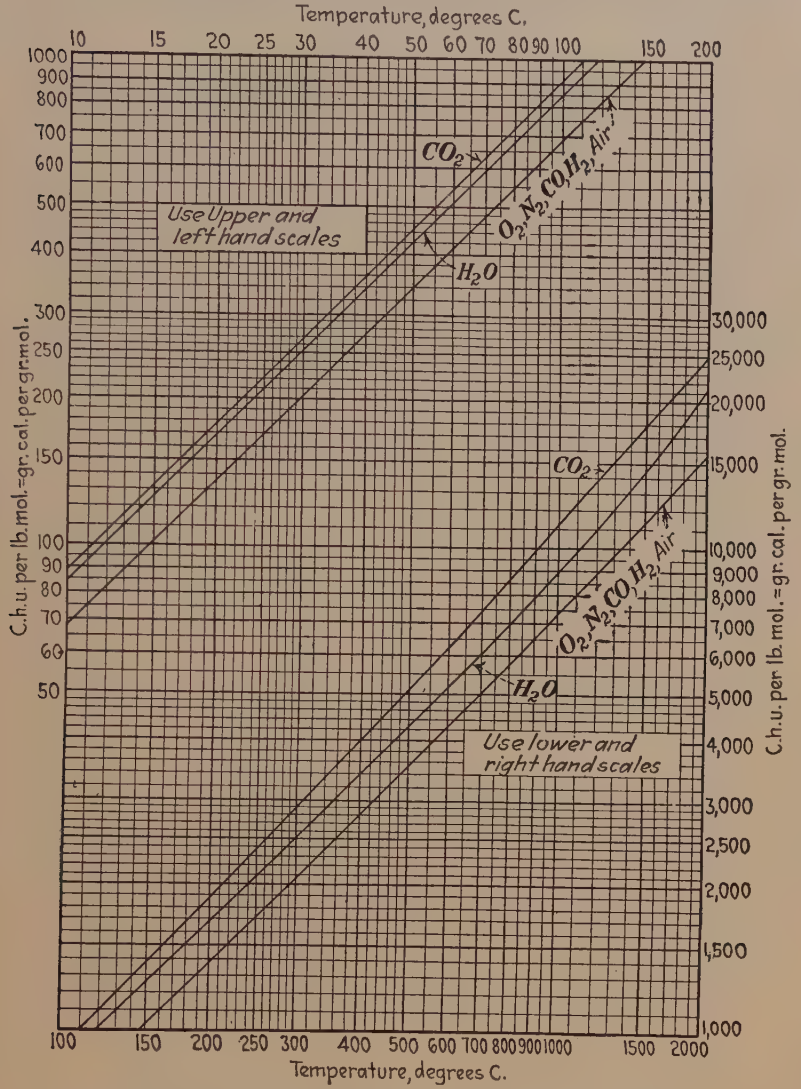

FIG. 1.—Sensible heat content of gases above 0°C., C.h.u.

[1] It is also recognized that the molal heat capacity of hydrogen ($6.5 + 0.0009T$) is less than that for nitrogen and oxygen ($6.5 + 0.0010T$). However, in most practical problems involving gases containing hydrogen, such as producer gas, the molal heat content of hydrogen may be assumed the same as that of the other diatomic gases, with little error.

Ratios and Conversion of Units.—In the main, chemistry is a science whose basic quantitative relationships are simple proportions. An appreciation of this fact greatly simplifies computa-

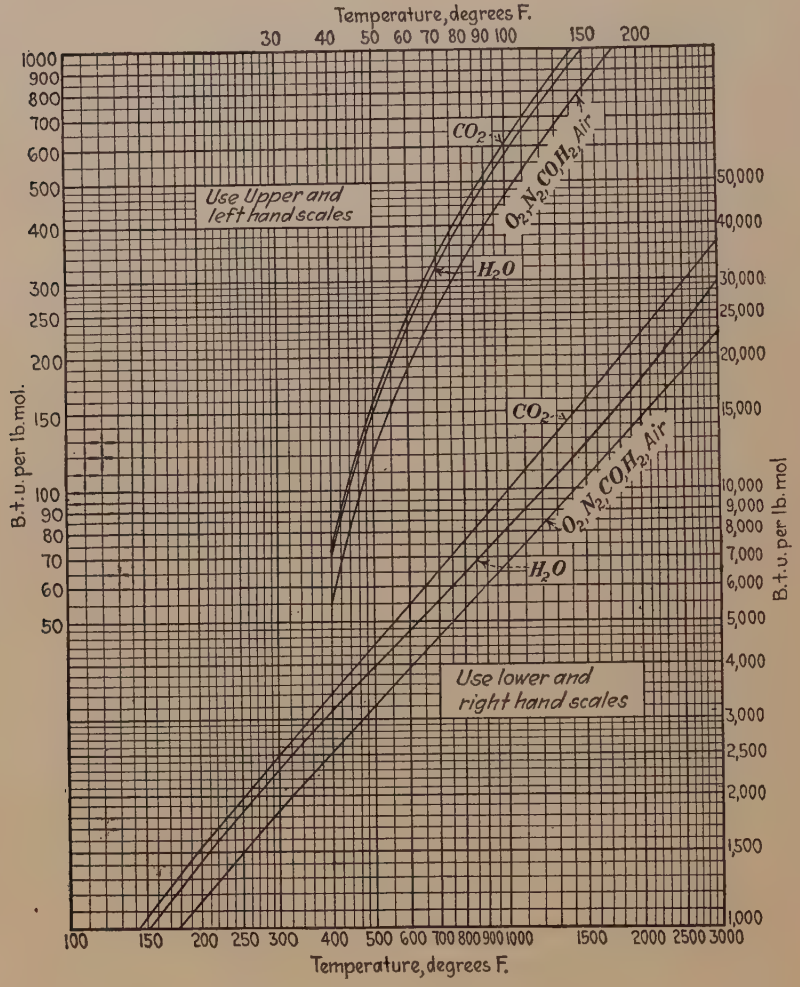

FIG. 2.—Sensible heat content of gases above 32°F., B.t.u.

tions, particularly the conversion of units from one system to another.[1] While this fact is emphasized repeatedly in the following chapters, a single illustration will not be out of place at this point. Assume that a sample of gasoline weighing 0.142 g.,

[1] See particularly pp. 139 and 140.

enclosed in a thin-walled sealed bulb, be introduced up through the mercury of a Torricellian barometer tube inverted in a dish of mercury, the whole jacketed at a temperature of 200°F. to insure complete vaporization of the gasoline. The height of the mercury in the tube above the level in the dish before the introduction of the bulb, corrected for the temperature of the mercury, was 752 mm. and after introducing and breaking the bulb was 664 mm. The volume of the vapor above the level of the mercury was 310 cc. It is required to deliver, to the intake of an internal-combustion engine, a mixture of this gasoline vaporized in air at a temperature of 100°F., at a concentration such that the partial pressure of the gasoline vapor is 12.5 mm. How many cubic feet of air-vapor mixture must be delivered to the intake per pound of gasoline vaporized?

Proportion offers perhaps the simplest method of solving this problem. The data show that at 200°F. and 752 − 664 = 88 mm. absolute pressure, 0.142 g. of gasoline vapor occupies the volume of 310 g. of water. By proportion, it is, therefore, obvious that, at 200°F. and 88 mm. pressure, 0.142 lb. of gasoline vapor will occupy the volume of 310 lb. of water, *i.e.*, 310/62.4 = 4.97 cu. ft. Hence, again by proportion, under the same conditions of temperature and pressure, 1 lb. of vapor would occupy 4.97/0.142 = 35.0 cu. ft. At the lower pressure of 12.5 mm.,[1] the volume of vapor is increased in inverse proportion to the pressures to 35.0(88/12.5) = 246.3 cu. ft. Due to the lower temperature, this is reduced in proportion to the absolute temperatures to 246.3(560/660) = 209 cu. ft. This is the volume of gasoline vapor–air mixture which must enter the intake in order to introduce 1 lb. of this particular gasoline as vapor if its partial pressure in the mixture is 12.5 mm.

It will be noted that such a method of attack avoids the necessity of conversion factors from one system to another and, furthermore, makes it possible easily and clearly to visualize the significance of each step of the computation, thereby greatly reducing the chances of errors.

Material and Energy Balances.—Because industrial stoichiometry is based on the laws of conservation of matter and of energy, the method of computation most frequently employed is

[1] Note that the volume of the gasoline depends on its partial pressure alone, and is independent of that of the air mixed with it and occupying the same volume.

the equation of input to output. Where the data are available, such a balance can be set up for each element involved, as well as for the energy effects. Furthermore, each of these equations is in such case independent of all the others. The most important factor in the technique of industrial stoichiometry is the mastery of the manipulation of balances of this sort.

Basis of Computation.—To insure clarity and accuracy of thinking, it is imperative to visualize exactly the thing under consideration. This thing or quantity about which one is talking is called the "basis" of computation. As will appear from the illustrations throughout this book, it is highly desirable to state the basis employed at the head of all computations and never to change it without indicating that this has been done. Changing bases in the midst of a computation is shifting gears with the clutch in and the throttle open. It is, perhaps, not impossible to do it, but, in general, the procedure is inadvisable.

At the end of each chapter will be found a number of numerical problems, the ready solution of which depends primarily upon the choice of a proper basis of computation.

Dependability of Results.—Because stoichiometric computations are based on laws of absolute validity, the dependability of the results can be limited only by the accuracy and completeness of the data. Thus, stoichiometric methods provide an excellent check on the reliability of industrial data from whatever source, making it possible to detect inconsistencies and errors and to avoid unjustifiable conclusions. Obviously, the data on which such computations are based must be collected with care. Samples taken for analysis must truly represent the average composition of the materials in question. Analyses must be made with accuracy. No sources of loss must be overlooked or neglected. When, however, these precautions have been taken and the data cross-checked by proper methods of computation and comparison, it becomes possible to have justifiable and well-founded confidence in the results and, therefore, in conclusions based upon them.

PROBLEMS

1. A rubber compound is analyzed by first extracting with acetone. The total acetone extract is found to be 4.32%. A portion of the rubber thus extracted is now analyzed for sulfur by oxidation and precipitation with barium sulfate in the usual way. The sulfur thus found in the extracted

material is 3.15%. There being no inorganic sulfur compounds in this particular sample, this figure represents the chemically combined sulfur in the rubber. What is the percentage of chemically combined sulfur in the original sample?

2. A furnace uses coal containing 3.3% moisture, 24.8% volatile combustible matter, 60.3% fixed carbon and 11.6% ash. The ashes removed from beneath the grate, when carefully sampled and analyzed, are found to contain 34.5% moisture (the ashes are wet down to prevent dusting), 4.7% volatile combustible matter and 18.2% fixed carbon, the remainder being ash. Of the total combustible matter in the fuel fired, what per cent is lost by falling through the grate with the ash?

3. A furnace fired with a coal containing 4.7% moisture, 24.3% volatile combustible matter and 61.4% fixed carbon and having a heating value of 14,800 B.t.u. per pound as fired yields an ash containing negligible moisture, 28% combustible matter substantially all carbon and the rest ash. Pure carbon has a heating value of 14,540 B.t.u. per pound. What percentage of the heating value of the fuel fired is lost as combustible matter falling through the grate with the ash?

4. A company buys its paper at a contract price of 11.4 cts. per pound, on a specification of 5% moisture and with an arrangement for price adjustment if the moisture content differs from this figure. A shipment of 13,682 lb. net weight is received, which is found upon careful sampling and analysis to average 7.86% moisture. What should be the billing price for the shipment?

5. If in the preceding problem arrangement had been made to adjust not only for the moisture content of the shipment but also for the difference in freight at a freight rate of 24 cts. per 100 lb., what should have been the billing price?

6. A tannery extracts Mangrove bark containing 4% moisture, 37% tannin and 23% soluble non-tannin material. The residue removed from the extraction tanks contains 62% moisture, 2.8% tannin and 0.9% soluble non-tannin material. What percentage of the tannin in the original bark remains unextracted in the residue?

7. Hemlock bark containing 6% moisture, 10.8% tannin and 8.2% soluble non-tannin is extracted by the countercurrent Shank's system. The extracted bark contains 0.95% tannin and 0.22% soluble non-tannin on a dry basis. If the cost of the original bark at the extraction plant is $26 per short ton, what is the raw-material cost of the tannin in the extract obtained?

8. Pure CO_2 is made by dissolving CO_2 from flue gas in a solution of an alkali carbonate and later boiling the CO_2 out of this solution, which is used over again. A plant of this sort has an average CO_2 content in its flue gases, as determined by an Orsat analysis, of 16.2%. The CO_2 content of the gases after leaving the absorbing towers is 9.5%. Of the total CO_2 entering the absorbers what per cent is dissolved?

9. Of the total CO_2 boiled out of the absorbing liquor in the plant of the preceding problem, 15% is lost in various ways, the remaining 85% being obtained as pure product. What per cent of the CO_2 in the original flue gas is obtained as final product?

10. A soap factory can sell its green soap with 25% moisture at 7 cts. per pound, or it can dry this soap down to a 5% water basis before marketing. The drying and other operations connected therewith cost a total of $1.20 per 1,000 lb. of water evaporated. What price can one afford to quote on the dried soap?

11. Chlorine gas containing 2.4% oxygen is flowing through an earthenware pipe. The gas is measured by introducing into it air at the rate of 115 cu. ft. per minute and further down the line, after mixing is complete, removing a second sample of the gas for analysis. The gas is now found to contain 10.85% oxygen. How many cubic feet of the initial gas were flowing per minute through the pipe?

CHAPTER II

FUELS AND COMBUSTION

Fuels may be divided into three classes, solid, liquid and gaseous. Although in industrial practice these types are differently employed, all combustion calculations are made in substantially the same way. The ultimate analysis of the components entering a system is the essential basis of measurement and computation. Consequently, the form of the fuel matters little.

Solid Fuels: Ultimate Analysis.—By ultimate analysis, solid fuels are found to contain carbon, hydrogen, sulfur, nitrogen, oxygen and ash, the mineral constituents (other than sulfur) being grouped together under the last head. The ultimate analysis is always reported in this way, oxygen being obtained by difference,[1] but may be reported upon either dry, "air-dried" or "as-fired" basis. It is not definitely known how the elements are combined, but it is convenient *for purposes of computation* to arrange the analytical results as follows:

1. Moisture (loss in weight at 105°C.).
2. Combined water, equivalent to the oxygen of the ultimate analysis.
3. Carbon.
4. Available or net hydrogen (other than that in moisture and combined water).
5. Sulfur and nitrogen (usually in small amounts).
6. Ash.

In fuel calculations, the sulfur and the nitrogen are often neglected, though present in amounts ranging from 1 to 3% or more. Since the hydrogen content is always in excess of that necessary to form water with the oxygen, it can be assumed for purposes of calculation that all the oxygen is present in the form of water of chemical combination; the excess of hydrogen is then termed "available" or "net," *i.e.*, combustible or burnable hydrogen.

[1] See, however, p. 36.

The ultimate analysis of coal is tedious and is often omitted, but, in order to obtain results of greatest value, should be made. Frequently, it is sufficient to know the carbon content only. It is often necessary, however, to estimate the composition of the fuel. Where the origin of the coal in question is known, it is usually safe to assume the ultimate analysis of its *combustible matter* to be identical with that of other samples from the same field. The ultimate analysis may also be estimated with fair precision from the proximate analysis and the heat of combustion.[1]

Proximate Analysis.—The usual approximate method of expressing the composition of a solid fuel is to assume it to consist of moisture, combustible matter and ash. Upon ignition in a covered crucible, under specified conditions of time and temperature, the fuel loses all its combined water and hydrogen and a large amount of carbon in the form of volatile hydrocarbons, leaving the ash and the residual carbon. This loss upon ignition after drying is called "volatile combustible matter." The combustible left after ignition is called "fixed carbon." The ash is the residue left from the complete combustion of the sample in the open air. The sum of moisture, volatile combustible matter, fixed carbon and ash is, therefore, 100%.

The proximate and ultimate analyses of a Pennsylvania coal are given as follows, both being on an "air-dried" basis:

	Proximate Per Cent		Ultimate Per Cent
Moisture	3.2	Carbon	79.90
Volatile combustible matter	21.0	Hydrogen	4.85
Fixed carbon	69.3	Sulfur	0.69
Ash	6.5	Nitrogen	1.30
		Ash	6.50
Total	100.0	Oxygen (by difference)	6.76
		Total	100.00

These two analyses must never be confused. From the proximate analysis it should not be concluded that the per cent of carbon in the coal is 69.3, but it should be remembered that the volatile matter contains carbon, enough in this case to make the total 79.90%. Likewise, the difference of 6.76% between the

[1] For methods of doing this see Walker, Lewis and McAdams, "Principles of Chemical Engineering," or Marks, "Mechanical Engineers' Handbook."

total of the ultimate analysis as directly determined and 100% should not be called combined water. This difference is assumed to be oxygen. The hydrogen equivalent to the 6.76 of oxygen is $6.76 \times 2/16 = 0.85$, leaving 4.00 as the available or net hydrogen, and $6.76 + 0.85 = 7.61$ as the total of combined water and moisture. Since, from the proximate analysis, it is already known that the moisture is 3.2, the combined water is 4.41%.

Liquid and Gaseous Fuels.—Stoichiometrically, these are handled in the same manner as solid fuels. Liquid fuels consist largely of carbon and hydrogen with little or no oxygen or ash. Natural gas contains compounds of carbon and hydrogen (mostly methane and ethane, but usually with appreciable amounts of higher hydrocarbons), together with small amounts of other gases (nitrogen, carbon dioxide, etc.). Manufactured or secondary gaseous fuels owe their calorific value to a number of gases which they contain, principally hydrogen, carbon monoxide and hydrocarbons. Here, however, owing to the large amount of nitrogen in some of them, this element cannot be neglected, as is so often done in combustion calculations dealing with solid fuels. The calculations pertaining to the preparation of one of the most important of these gaseous fuels are treated in Chap. III on Gas Producers.

Whereas the analyses of both solid and liquid fuels are almost always reported as weight per cent, those of all gases, including both fuels and combustion products, are normally reported by volume per cent, which is identical with mol per cent. Wherever analyses are otherwise reported, it is imperative to state the fact.

In reporting nitrogen, most or all of which usually comes from the air, the argon (and other noble gases) present in air to the extent of 1% is included with the nitrogen. Working by volume per cent, this is entirely allowable, since both elements take no part in ordinary combustion reactions.

Heats of Combustion.—The heats of combustion of some of the more important compounds found as components of fuels are given in the following table.

MOLAL HEATS OF COMBUSTION AT CONSTANT PRESSURE AT 20°C.

In gram calories per gram mol = C.h.u. per pound mol

Fuel	Higher heating value, water condensed	Lower heating value, water uncondensed
Hydrogen (H_2)	68,300	58,000
Carbon (C to CO_2)	97,000	97,000
Carbon monoxide (CO to CO_2)	68,000	68,000
Methane (CH_4)	212,000	191,000
Ethane (C_2H_6)	371,000	349,500
Ethylene (C_2H_4)	336,000	315,000
Acetylene (C_2H_2)	312,000	301,500
Propane (C_3H_8)	529,000	487,000
Propylene (C_3H_6)	496,000	464,500
Benzene (C_6H_6)	783,000	751,500
Sulfur (S to SO_2)	69,300	69,300

Elementary Combustion Calculations.—If pure carbon (charcoal or coke, free of hydrogen) could be burnt with the theoretical amount of air, CO_2 would replace the O_2 in the air, mol for mol, and the analysis of the combustion gases would necessarily be 21.0% CO_2 and 79.0% N_2.[1] If, on the other hand, 50% excess air be used, only two-thirds of the O_2 in the air would be replaced by CO_2, the analysis of the flue gas under such conditions being 14.0% CO_2, 7.0% O_2 and 79.0% N_2. The formation of CO, due to incomplete combustion or oxidation of the carbon, involves another step in calculation, because the reaction, $2C + O_2 = 2CO$, shows that 2 mols of CO are obtained for each mol of O_2. Suppose this same coke is burnt under such conditions that 75% of the carbon burns to the monoxide, the rest to dioxide, there being no excess air. This means that on burning 100 atoms of carbon there will be formed 75 mols of CO for every 25 mols of CO_2, sequiring, therefore, 37.5 mols of O_2 for the former and 25 for the latter gas, the total O_2 consumption being 62.5 mols. For every 100 mols of air, there are 79 of N_2 which must appear in the combustion gases. Of the 21 mols of O_2 in this air, the amount going to CO is in the proportion of 37.5:62.5, or 12.6 mols, forming 25.2 mols of CO. The rest, 8.4 mols, yields the same number of mols of CO_2. The following table summarizes the data:

[1] Throughout this book air is assumed to contain 21.0% O_2 by volume. This is perhaps high by a few hundredths of a per cent.

Component	Mols per 100 of air	Fraction of total	Per cent of gas
N_2	79.0	79.0/112.6	70.15
CO	25.2	25.2/112.6	22.4
CO_2	8.4	8.4/112.6	7.45
Total combustion gases	112.6	.....	100.0

The presence of hydrogen in the fuel involves still another point. Pure hydrogen when burnt with theoretical air would, in effect, remove the oxygen from the air as water. The combustion gases would be water vapor and nitrogen, provided they are at some temperature above the condensation point of the water contained in them. The gas analysis, however, does not show the presence of water, as it is condensed before and during the analysis, the resulting figures being on a dry basis. The analysis is, therefore, 100% N_2. With excess air, the corresponding oxygen would appear in the gas, with a decrease in the percentage of nitrogen.

Consider a mol of methane burning with 100% excess air. The equation for the combustion may be written,

$$CH_4 + 2O_2 + (2O_2) = CO_2 + 2H_2O + (2O_2).$$

The $(2O_2)$ represents the excess oxygen used. Thus there would be obtained 1 mol CO_2, 2 mols H_2O and 2 mols O_2. The nitrogen which came into the furnace along with the oxygen is $4 \times 79/21 = 15.05$ mols, giving a total of 20.05 mols of wet gas, but only 18.05 mols of water-free gas. In the latter, the CO_2 will be 1/18.05, or 5.54%; the O_2, 2/18.05, or 11.08%; and the N_2, 15.05/18.05, or 83.38%.

When hydrogen is present in the fuel and CO appears in the gases, there is a combination of the above conditions. A theoretical water gas, *i.e.*, an equimolal mixture of CO and H_2, burning with 30% excess air but with only 90% of the CO being converted to CO_2, would be an example. The 0.5 mol of CO and of H_2 contained in a mol of this water gas would each require 0.25 mol of O_2, a total of 0.5 mol for theoretical combustion. Using 30% excess, the O_2 employed would be $1.3 \times 0.5 = 0.65$ mol. The oxygen present in the combustion products may be considered as made up of two kinds; first, the 0.15 mol used in excess of that required for theoretically perfect combustion, and, second,

10% of the 0.25 mol theoretically required by the CO but not used in the combustion. It is now easy to find the amounts of the various gases and the percentage composition.

	Mols	Fraction of total	Per cent
90% of 0.5 mol CO =	0.45 CO_2	0.45/3.12	14.4 CO_2
10% of 0.5 mol CO =	0.05 CO	0.05/3.12	1.6 CO
0.15 + 0.10 (0.25) =	0.175 O_2	0.175/3.12	5.6 O_2
0.65 (79/21) =	2.445 N_2	2.445/3.12	78.4 N_2
Total water-free gas	3.12		100.0
0.5 mol H_2 =	0.50 H_2O		
Total gas	3.62		

Coal and fuel oil contain carbon and hydrogen in proportions which are not in simple molal ratios. The methods of calculation are similar to the above. Computation of the analysis of the products of combustion of a fuel oil containing 84.6% C, 10.90% H and 2.87% O by weight, when burnt with 20% excess air, assuming that all the hydrogen is converted to water, 95% of the C burning to CO_2 and the rest to CO, will serve as an illustration.[1]

Since the composition of the oil is given on a weight basis and the gas analysis will be on a molal basis, it is best to convert the analysis of the oil to a molal basis. Consider 100 lb. of the oil and find the number of atoms or mols of each constituent.

$$84.6/12 = 7.05 \text{ atoms C}$$
$$10.90/2.02 = 5.40 \text{ mols } H_2$$
$$2.87/16 = 0.18 \text{ atom O}$$

The 0.18 atom of O is equivalent to an equal number of mols of H_2. Hence the oil contains $5.40 - 0.18 = 5.22$ mols of net H_2, requiring 2.61 mols of O_2 for combustion. With 20% excess air, the O_2 used is $(7.05 + 2.61)\,1.2 = 11.59$ mols and the corresponding N_2, $11.59(79/21) = 43.6$ mols. The actual excess O_2 is 20% of $(7.05 + 2.61)$, or 1.93 mols, and the total is this number plus that unused by the carbon due to its burning only to CO. This latter is $0.05(7.05)/2 = 0.18$ mol, giving a total O_2 of 2.11 mols. The results may now be arranged as previously, leaving out the water vapor formed.

[1] Ash, nitrogen or other elements present are here neglected.

	Mols	Fraction of total	Per cent
CO_2: 0.95×7.05 =	6.70	6.70/52.76	12.7
CO: 0.05×7.05 =	0.35	0.35/52.76	0.6
O_2: $1.93 + 0.18$ =	2.11	2.11/52.76	4.0
N_2	43.6	43.6/52.76	82.7
Total	52.76	.....	100.0

These illustrations show how, for any given fuel, the gas analysis is definitely determined by combustion under fixed conditions. It follows that, for a given fuel to yield a gas having a known composition, the combustion taking place must be of a definite character. It is now necessary to attack the problem most frequently met in combustion calculations, that of determining the character of the combustion from the analyses of fuel and combustion products.

The purpose of the following illustrations is to show the possibility and method of computing net hydrogen burnt from oxygen disappearance in the flue gas analysis. Mathematically, the reasoning is equivalent to setting up a nitrogen balance, equating the nitrogen in the flue gas to that in the air employed and using this equation to solve for the total oxygen which went into the flue gas from the air. This is followed by an oxygen balance, solving for the otherwise unknown amount of oxygen going to burn hydrogen to form water.

Significance of Flue-gas Analysis: Illustration 1.—The flue gas from a certain furnace burning a fuel of negligible nitrogen content is found by analysis to contain 12% CO_2, 7.5% O_2 and 80.5% N_2. What conclusions can be drawn from these figures?

Take as a basis for computation 100 mols of this gas as analyzed. As appears from the subjoined table, the analysis shows the presence of 19.5 mols of O_2. The nitrogen came, however, from the air used for combustion and hence brought with it 21.4 mols of O_2. Oxygen has, therefore, disappeared from the gas as analyzed and this disappearance of 1.9 mols of O_2 must be caused by and correspond to the combustion of the net hydrogen in the fuel. The hydrogen burnt is, therefore, 3.8 mols. The water formed by this combustion, together with any other which may have been present, was condensed before and during the analysis.

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Component	Mols	Mols O_2
CO_2	12.0	12.0
O_2	7.5	7.5
N_2	80.5	
Total	100.0	19.5 O_2 accounted for
	80.5(21/79) =	21.4 O_2 from air
O_2 unaccounted for by analysis =		1.9 O_2 disappearance
$\therefore$ H_2 burnt to H_2O = 2(1.9) =		3.8 H_2O from combustion

This 100 mols of dry gas contains 12 atoms, or 144 lb., of C, which came from the fuel and hence represents the carbon burnt, though it does not include any carbon left as unburnt combustible mixed with the ash or elsewhere. This carbon burnt was accompanied by 3.8 mols, or 7.65 lb., of net hydrogen in the fuel. Hence, for each pound of carbon burnt, the dry flue gas was 100/144, or 0.695 mol, or 249.4 cu. ft. under standard conditions. Furthermore, except for water in the air or fuel used, the total flue gas was 103.8/144 = 0.722 mol, or, at standard conditions, 259 cu. ft. per pound of carbon burnt.

Since the O_2 used for combustion was 12.0 + 1.9 = 13.9 mols, while an excess of 7.5 was present, the per cent excess oxygen is (7.5/13.9)100 = 54%. This is, of course, identical with per cent excess air. This figure, however, makes no allowance for unburnt combustible, if present.

It is worth noting that all this information is secured from the flue-gas analysis and nothing else. It is unnecessary to know whether the fuel is solid, liquid or gaseous—merely that it is nitrogen-free.

One of the most serious sources of heat loss in many furnace operations is the sensible heat in the stack gases, caused by the difficulty and expense of cooling these to low temperatures. Such losses are obviously dependent upon the amount of the gases. Direct measurement of these is almost always impossible and their amount is determined by making a flue-gas analysis such as the above, computing therefrom, by the method just shown, the quantity of gas per pound of carbon burnt, and finding the total quantity of gas by multiplying by the fuel burnt times its known carbon content, the fuel being measured directly.

Because this is the normal method of measurement and control of heat losses up the stack, it is important to master the technique of calculation. The principle remains unchanged, but certain minor modifications are frequently met which will be explained in the illustrations. Of these, the first is due to incomplete oxidation of carbon to CO_2, the second involves correction for water from various sources, the third allows for nitrogen in the fuel, the fourth for sulfur and the fifth for unburnt combustible left in the ashes and furnace refuse. Others less important will be merely mentioned. Furthermore, to solve these problems the results of the flue-gas analysis must be tied in with the data on the fuel. All but the first of the points mentioned will be discussed only in connection with this last step.

Illustration 2.—Take the case of a flue gas containing 11.3% CO_2, 1.2% CO, 7.7% O_2 and 79.8% N_2 to illustrate incomplete oxidation in the combustion gases themselves. Tabulate these figures as before:

Basis.—100 mols of gas as analyzed.

Component	Mols	Atoms C	Mols O_2
CO_2	11.3	11.3	11.3
CO	1.2	1.2	0.6
O_2	7.7	....	7.7
N_2	79.8		
Total	100.0	12.5	19.6 O_2 accounted for
79.8(21/79) =			21.21 O_2 from air
O_2 unaccounted for by analysis =			1.61 O_2 disappearance
∴ net H_2 burnt to H_2O = 2(1.61) =			3.22 H_2O from combustion

It should be noted that the total carbon, the only significant thing in a carbon balance such as will be used, comes from two components instead of one as before, while oxygen appears in three rather than two.

On this basis, the carbon burnt is 12.5(12) = 150 lb. Hence, the dry flue gas per pound of carbon burnt is 0.667 mol, or 239.3 cu. ft. under standard conditions.

Per Cent Excess Air.—In computing excess air it must be remembered that the combustion reactions did not complete themselves, some unburnt CO remaining. Hence, some of the oxygen present as such is not actually in excess of that required for perfect combustion of the fuel burnt. The term "excess air" is defined as the amount of air used above that theoretically needed for complete combustion (*i.e.*, to burn carbon and hydrogen, or compounds of the two, to carbon dioxide and water). The per cent excess air is the ratio of the excess to the theoretical amount, multiplied by 100. It is most conveniently interpreted in terms of "oxygen" instead of "air." Normally, the flue-gas analysis furnishes the only data from which it may be calculated.

The oxygen present in the flue gas (7.7 mols) is not the true excess, since, by definition, complete combustion of carbon to CO_2 is required. This oxygen must be diminished by 0.6 mol, which is the amount required to burn the CO present to CO_2. The oxygen necessary for combustion is 12.5 mols for the carbon and 1.61 mols for the hydrogen, and the total oxygen used is 21.21 mols. The per cent excess air (or oxygen) may be found in several different ways:

$$(100)\frac{\text{Unnecessary}}{\text{Total} - \text{Unnecessary}} = \frac{100(7.1)}{21.21 - 7.1} = 50.3\%.$$

$$(100)\frac{\text{Unnecessary}}{\text{Necessary}} = \frac{100(7.1)}{12.5 + 1.61} = 50.3\%.$$

$$(100)\frac{\text{Total} - \text{Necessary}}{\text{Necessary}} = \frac{100(21.21 - 14.11)}{14.11} = 50.3\%.$$

It will be noted that these are not independent methods, but merely various arrangements of the same data.

Interrelations of Flue-gas and Fuel Analyses: Illustration 3.—A furnace burns a coke containing, as fired, 3.5% moisture and 14.5% ash. The moisture content of the air is negligible. The flue gases from this furnace contain 16.3% by volume of CO_2, 0.4% CO, 4.3% O_2 and, by difference, 79.0% N_2. Combustible matter left in the ash is negligible. What is the quantity of air and of flue gas per pound of coke fired?

It is a mistake to start by trying to compute directly the quantities desired, but the flue-gas data should first be tabulated and analyzed exactly as in the preceding cases.

Basis.—100 mols of dry flue gas.

Component	Mols	Atoms C	Mols O_2
CO_2	16.3	16.3	16.3
CO	0.4	0.4	0.2
O_2	4.3	....	4.3
N_2	79.0		
Total	100.0	16.7	20.8 O_2 accounted for
79.0(21/79) =			21.0 O_2 from air
			0.2 O_2 disappearance

$\therefore$ net H_2 burnt = 2(0.2) = 0.4 = H_2O from combustion
Pounds C burnt = 16.7(12) = 200.4 lb.
Pounds H_2 burnt = 0.4(2) = 0.8 lb.

Total weight of net combustible burnt = 201.2 lb.

The analysis of the coke shows that the combustible in it is 82.0% of the total, since 18.0% is the combined percentage of water and ash. This combustible is composed of carbon and hydrogen, since the combined oxygen has been driven out in the coking operation. The flue-gas analysis shows, however, that the weight ratio of C:H in the combustible is 200.4:0.8 or the fraction of H in it is 0.8:201.2. Therefore, the hydrogen in the coke, obtained from the proportion, $0.8:201.2::x:82.0$, is $82.0(0.8/201.2) = 0.33\%$ and the carbon is $82.0 - 0.33 = 81.67\%$. The fuel analysis can now be tabulated as follows:

Basis.—100 lb. of coke as fired.

Component	Pounds	Mols or atoms
Moisture	3.5	0.195
C	81.67	6.82
H_2	0.33	0.16
Ash	14.5	
Total	100.0	

These two tabulations make it possible to compute the quantities required.

1. *Cubic feet of air used per pound of coke fired.* It is obvious that carbon connects the flue-gas analysis with that of the fuel, while nitrogen connects the flue-gas analysis with the air

employed. However, the easiest way of carrying out the carbon and nitrogen balances involved is by the use of ratios. Thus, the flue-gas data show that in it the ratio between nitrogen and carbon is 79.0:16.7. If, therefore, the atoms of carbon per pound of fuel, 0.0682, be multiplied by this ratio, the nitrogen per pound of fuel is obtained. Since, however, this nitrogen all came from the air, and since this air contains 79% of N_2, the mols of air can be obtained by multiplying by 100/79. This figure can, of course, be converted to cubic feet under standard conditions by multiplying by the pound-molal volume. These operations are most readily carried out and the individual steps visualized as follows:

$$\frac{\text{Atoms C}}{0.0682} \left| \frac{\text{Mols } N_2}{79.0} \right| \frac{\text{Mols air}}{100} \left| \frac{359}{} \right. = \frac{}{16.7} \left| \frac{}{79} \right. = 146.5 \text{ cu. ft. air at S. C.}$$

It is merely fortuitous that the nitrogen content of this flue gas is identical with that of air, so that the quantity 79 appears in both the numerator and the denominator.

2. *Cubic feet of flue gas per pound of coke fired.* By a line of reasoning entirely analogous to that of the preceding paragraphs, it is seen that the dry flue gas per pound of coke is obtained by multiplying the atoms of carbon per pound of fuel by the ratio of dry flue gas to CO_2 in it, 100:16.7, giving 0.408 mol. On the other hand, the flue gas contains water vapor from two sources, partly from combustion of the net hydrogen and partly from the moisture in the fuel. On the basis of 100 mols of dry flue gas, the water from the net hydrogen has already been computed as 0.4 mol. The water in the fuel must, however, be obtained by a carbon balance, because carbon is the thing which ties flue gas and fuel together. As before, the easiest way to set up such a carbon balance is to use a ratio. Inspection of the fuel analysis shows that it contains water and carbon in the ratio 0.195:6.82. If, therefore, the carbon content of the flue gas, 16.7, be multiplied by this ratio, the water in the flue gas coming from the moisture in the fuel, 0.48 mol, is obtained. This makes the total water content of the flue gas 0.9 mol. The total amount of flue gas per pound of coke is, therefore

$$\frac{\text{Atoms C}}{0.0682} \left| \frac{\text{Mols wet gas}}{100.9} \right| \frac{359}{} = \frac{}{16.7} \left| \frac{}{} \right. = 148 \text{ cu. ft. at S. C.}$$

This volume must, of course, be corrected for temperature and pressure.

In this case, the tabulation on the basis of 100 lb. of coke can be avoided. Returning to the tabulation on a flue-gas basis, it is seen that the net combustible per 100 mols of dry flue gas is 201.2 lb. Since the fuel contains 82% of such combustible, the coke burnt per 100 mols of dry flue gas must be 201.2/0.82 = 245.2 lb. Its water content is 0.035(245.2) = 8.57 lb. = 0.48 mol. This is another method of obtaining this figure.

Heat Losses in Stack Gases: Illustration 4.—Using the data of the previous problem, find the amount of sensible heat in the hot stack gases per pound of coke burnt. These gases leave the furnace at a temperature of 560°F. The coke and air used for combustion are at 50°F.

The heat loss is most easily found by multiplying the number of mols of each of the gases, CO_2, CO, O_2, N_2 and H_2O, by the difference in their respective molal heat contents at 560°F. and 50°F. since, to recover all the available heat, the products of combustion must be cooled from the former temperature to the latter. The values are read from Fig. 2 (p. 6), the diatomic gases being grouped together for this purpose, since their molal heat contents are identical. Retabulation of the gas analysis and incorporation of the heat values give the following table of data:

Basis.—100 mols of dry gas.

Gas	Mols	Heat content, B.t.u.		Difference = heat loss per mol	Total loss, B.t.u.
		At 560°F.	At 50°F.		
CO_2	16.3	5,100	160	4,940	80,500
CO	0.4				
O_2	4.3	3,650	120	3,530	295,500
N_2	79.0				
H_2O	0.9	4,500	150	4,350	3,900
Total	100.9	.....	...	.....	379,900

The first of these four additional columns gives the heat contents, at 560°F., of the gases shown in the first column of the table. The second column gives the heat contents at 50°F., the third the difference between the first two, or the heat loss per

mol of the gas in question. The fourth column is the product of this difference and the number of mols of the gas shown in the second column of the table. The result shows that 379,900 B.t.u. is the sensible heat retained by 100 mols of dry or 100.9 mols of total flue gas, *i.e.*, by the total gas corresponding to 16.7 atoms of C burnt. Using this ratio, the heat loss per pound of coke fired is 0.0682(379,900/16.7) = 1,550 B.t.u.

Unburnt Combustible.—In the previous illustrations the fuel was assumed to be completely gasified by combustion, an assumption usually justified when oil and fuel gases are under consideration and often when solids are the combustible material. This assumption may, however, lead to serious error in the case of the latter, because the furnace ashes often contain a considerable amount of combustible matter. Since the mineral constituents of the fuel are known chemically as *ash*, it is common practice to designate the ashes removed from the furnace as "refuse," which may include varying amounts of unburnt combustible matter. This latter is generally one of two kinds, depending upon the type of grate and the method of firing employed. With some grates and coals the finer particles of fuel fall through before any appreciable heating has taken place, but the refuse is otherwise well burnt out. Here the combustible matter in the refuse is of the same composition as the original fuel. With other types, all the fuel is thoroughly coked before any can escape into the ash pit, so that any unburnt combustible is essentially carbon. From the character of the grate and coal and an examination of the refuse it is usually possible to decide to which class the case belongs. There are, of course, gradations between these two extremes and, if the amount of unburnt matter in the ashes appears large enough to affect the combustion calculations, a complete analysis should be made.

Illustration 5.—If a coal with a heating value of 14,350 B.t.u. per pound contains 37.0% volatile matter, 40.5% fixed carbon and 8.9% ash and the refuse left after combustion contains 7.4% volatile matter, 8.25% fixed carbon and the rest ash, it can be seen by inspection that this is a case of unburnt coal actually falling through the grate, since the ratio of fixed carbon to volatile matter in the fuel, 40.5/37.0 = 1.094, is practically the same as the ratio, 8.25/7.4 = 1.114, in the refuse. The ash in the original fuel passes through the grate unchanged and can be used as the basis for any comparison. The ratio, pounds of combustible

per pound of ash, in the fuel is $(37.0 + 40.5)/8.9 = 8.71$, whereas in the refuse it is $(7.4 + 8.25)/(100 - 7.4 - 8.25) = 0.186$. Consequently, the ratio of the amount left to the total amount, $0.186/8.71 = 0.021$, represents that fraction of the coal not burnt and therefore the fraction of the heating value lost due to this cause.

Suppose, however, the same coal be burnt under conditions such that analysis of the dry refuse shows 0.4% volatile matter and 15.6% fixed carbon. Here it is apparent that the fuel has been thoroughly coked but the coke incompletely burnt.[1] Since in the process of coking, the fuel has lost some of its combustible and its corresponding heating value, a direct comparison cannot be made as above. However, the heating value of the carbon in the refuse may be found as follows:

Basis.—1 lb. coal.

Pounds ash	Pounds C in refuse	Atoms C	C.h.u. available	
0.089	16		97.000	1.8
	84	12		

= 247 B.t.u. loss per pound coal

The loss in the heating value is, therefore, $(247/14{,}350)\ 100 = 1.72\%$.

Illustration 6.—A coal contains 4% moisture, 23% volatile matter, 64% fixed carbon and 9% ash and has a heating value of 14,100 B.t.u. per pound. Determination of the carbon in the coal shows it to be 79%. The refuse removed from the ash pit of a grate-fired furnace using this coal contains 62% moisture (due to wetting down of the ashes by the hose to lay dust), 3% volatile combustible matter, 11% fixed carbon and 24% ash. Estimate the per cent of the heating value of this coal lost in the furnace as unburnt combustible and the per cent of carbon fired which remains in the refuse.

Solution.—The combustible matter in the refuse is not wholly coked fuel, as is evidenced by the presence of considerable volatile matter in it, neither is it wholly uncoked coal, since the ratio of fixed carbon to volatile in the fuel, $64/23 = 2.78$, is not the same as that, $11/3 = 3.67$, obtained from the refuse. It is fair to assume that some wholly unburnt coal has dropped through the grate, the amount of this being measured by the volatile matter in

[1] Even pure carbon shows a trace of volatile matter as the analysis is carried out.

the refuse, and that additional coal, coked completely in passing over the grate, has not had all the carbon burnt out of it. These are reasonable assumptions, since in the actual coking process there is little loss of volatile matter until a certain temperature is reached, but when decomposition starts it is completed in a relatively narrow temperature range without much further heat supply and, on a furnace grate, in a relatively short time.

The volatile combustible matter in the refuse is, obviously, a measure of and proportional to the uncoked coal. Therefore the loss in heating value due to uncoked coal is estimated as follows:

Basis.—1 lb. coal as fired.

$$\frac{\text{Pounds ash}}{0.09} \Big| \frac{\text{Pounds volatile in refuse}}{3} \Big| \frac{100}{24} \Big| \frac{}{23} = 0.049 \text{ lb. uncoked coal in refuse}$$

with a corresponding loss in heating value of (0.049)14,100 = 690 B.t.u.

The total fixed carbon in the refuse is made up of that due to uncoked coal as well as that from the coke present. The former, expressed per 100 lb. of refuse, is $3 \times 64/23 = 8.35$, whereas—the total being 11—the difference, 2.65, is that corresponding to the coke present. That is, the pounds of carbon in the refuse are $0.09(2.65/24) = 0.0099$ per pound of coal and the corresponding heating value is $(0.0099/12)(97{,}000)1.8 = 145$ B.t.u. Therefore, the total per cent loss is $(690 + 145)(100)/14{,}100 = 5.92\%$.

In these computations the presence of moisture in the refuse introduces no complications, since ratios alone are used to transform from one basis to another.

If there is 0.049 lb. of uncoked coal in the refuse, there is $0.049(0.79) = 0.0387$ lb. of carbon in it. The total carbon unburnt is $0.0387 + 0.0099 = 0.0486$ lb., or $100(0.0486/0.79) = 6.15\%$ of the carbon in the coal.

Illustration 7.—In order to make inert gas (which for the purpose in hand must contain not over 4% O_2), a plant intends to burn in a special furnace its regular boiler coal. This contains 4.2% moisture and, on the dry basis, 79.90% C, 4.85% H, 0.69% S, 1.26% N, 7.60% O and 5.7% ash. Before being used, the gas must be cooled to 30°C. Air for the combustion is at an

average temperature of 80°F., and an average relative humidity of 50%; 1,200 cu. ft. of cooled gas must be furnished per minute. Assume the carbon in the fuel to be completely burnt.

1. How many pounds of coal per hour must be burnt to furnish the gas?

2. How many gallons of water will be condensed out of the gas and removed in the cooler per hour?

Solution.—The only condition given for the gas analysis is that it shall contain not more than 4% O_2. It will be assumed that the gas contains the maximum per cent of oxygen allowable, but that this per cent will be that ordinarily determined, *i.e.*, of the dry gas. Since the gas will contain water vapor from both the air and the coal, the true percentage will be somewhat less than 4%. This, of course, will be on the safe side. It will further be assumed that all the carbon in the coal burns to CO_2; there is no CO formation. As usual, sulfur and nitrogen in the coal will be neglected in the calculations. However, in order to tie up the amount of coal and the quantity of air used with the amount of gas to be produced, more information than that given concerning the gas analysis must be at hand. Accordingly, the gas analysis will be calculated.

Basis.—100 lb. of dry coal.

	Pounds	Mols or atoms[1]	O_2 required
C	79.9	6.66	6.66
H_2	4.85	2.40	
O_2	7.60	0.24	
Net H_2	.....	2.40 − 0.48 = 1.92	0.96
Total	.....	.....	7.62

[1] When a column in one of these tables is headed "Mols or atoms" the symbol of the element in the left-hand column tells which it is. Thus, if the symbols C, H, O, etc. appear, the figures represent atoms but if they read H_2, O_2, etc. the values are in mols.

Let x be the number of mols of O_2 used in excess. The dry gas is to have in it only CO_2, O_2 and N_2 and the amounts of these will be:

Gas	Mols
CO_2	6.66
O_2	x
N_2	$(7.62 + x)(79/21)$
Total	$6.66 + x + (7.62 + x)(79/21)$

The requirement is that the volume (or mol) per cent of O_2 must be 4.0. Hence,

$$\frac{100x}{6.66 + x + (7.62 + x)(79/21)} = 4.0,$$

whence $x = 1.74$ mols. This gives the gas analysis:

Gas	Mols	Per cent
CO_2	6.66	15.3
O_2	1.74	4.0
N_2	35.10	80.7
Total	43.50	100.0

1. *Pounds of coal burnt per hour.* The gas analysis now known, its carbon content can be used in a "carbon balance" between the gas and coal to calculate the amount of the latter. The gas is certainly saturated with water vapor at 30°C. ($p = 31.5$ mm.), the excess water being condensed out in the cooler. It will be shown under paragraph 2 that this is so.

Basis.—1 hr.

$$\frac{\text{Cubic feet gas}}{(1{,}200)(60)} \left| \frac{\text{Dry gas}}{728.5} \right| \frac{\text{At S. C.}}{273} \left| \frac{\text{Mols}}{359} \right| \frac{\text{Atoms C}}{15.3} \left| \frac{\text{Pounds dry coal}}{100} \right| \frac{100}{95.8} = 415 \text{ lb. coal per hour}$$
$$\qquad\qquad 760 \qquad\quad 303 \qquad\quad 100 \qquad\quad 6.66$$

2. *Gallons of water condensed per hour.* The amount of water condensed out of the gas is the difference between the water content of the gas entering and that leaving the cooler. Water in the gas comes from two sources: that in the air used for combustion, and that in the coal burnt. The vapor pressure of water at 80°F. is 1.03 in., and if the air used is 50% saturated, the pressure of the water vapor in it is 0.52 in. The dry air pressure is 29.40 in. if normal barometric pressure is assumed. The molal ratio of water to dry air is 0.52: 29.40. Therefore, in the air there will be

$$\frac{\text{Cubic feet gas}}{(1{,}200)(60)} \left| \frac{\text{Dry gas}}{728.5} \right| \frac{\text{At S. C.}}{273} \left| \frac{\text{Mols flue gas}}{359} \right| \frac{\text{Mols } N_2}{80.7} \left| \frac{\text{Mols air}}{100} \right| \frac{0.52}{29.40} = 3.13 \text{ mols } H_2O$$
$$\qquad\qquad 760 \qquad\quad 303 \qquad\quad 100 \qquad\quad 79$$

From the moisture alone in the coal, the water is

$$415 \times 0.042/18 = 0.97 \text{ mol } H_2O.$$

Water is also produced from the hydrogen in the coal; 100 lb. of dry coal contain 2.40 mols of total H_2, which upon combustion give 2.40 mols H_2O.

$$\frac{\text{Pounds coal per hr.}}{415} \left| \frac{\text{Pounds dry coal}}{95.8} \right| \frac{2.40}{100} = 9.55 \text{ mols } H_2O \text{ from hydrogen in the coal}$$
$$\left| \frac{95.8}{100} \right|$$

This gives a total of $3.13 + 0.97 + 9.55 = 13.65$ mols of water contained in the gas going to the cooler per hour.

If the gas were saturated at 30°C., it would contain

$$\frac{\text{Cubic feet gas}}{(1,200)(60)} \left| \frac{\text{At S. C.}}{273} \right| \frac{\text{Mols}}{359} \left| \frac{31.5}{760} \right. = 7.50 \text{ mols } H_2O \text{ per hour}$$
$$\left| \frac{273}{303} \right|$$

As this is less than the quantity entering, it is saturated when leaving, and water must have condensed out to the extent of $13.65 - 7.50 = 6.15$ mols. As there are 8.33 lb. of water to a gallon,

$$6.15(18)/8.33 = 13.3 \text{ gal. of } H_2O \text{ condensed per hour.}$$

Illustration 8.—At one stage in the burning of an oil-fired kiln, the kiln gases issue at 1250°F., and contain 11.6% CO_2 and 6.0% O_2. The analysis of the oil may be taken as 84.6% C, 10.90% H, 1.63% S and 2.87% O, and the specific gravity is 0.924. At this stage of the process:

1. What is the per cent excess air used in burning the oil?
2. How many cubic feet of air at 75°F. are used per gallon of oil?
3. How many cubic feet of kiln gas are formed per gallon of oil?
4. What is the dew point of the kiln gas?

Solution. *Basis.*—100 mols of dry kiln gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	11.6	11.6	11.6
O_2	6.0	....	6.0
N_2 (by difference)	82.4		
Total	100.0	11.6	17.6 O_2 accounted for
82.4(21/79) =			21.9 O_2 from air
			4.3 O_2 disappearance

$\therefore$ H_2 burnt = 2(4.3) = 8.6 = H_2O from combustion.

Basis.—100 lb. oil.

	Pounds	Mols or atoms
C	84.60	7.05
H_2	10.90	5.40
O_2	2.87	0.09
Net H_2	5.40 − 0.18 =	5.22

1. *Per cent excess air.*

$$100(6.0)/(21.9 - 6.0) = 37.7\% \text{ excess air.}$$

2. *Cubic feet of air at 75°F. used per gallon of oil.*

$$1 \text{ gal. oil} = 8.33(0.924) = 7.69 \text{ lb.}$$

$$\frac{\text{Pounds oil}}{7.69} \left| \frac{\text{Atoms C}}{7.05} \right| \frac{\text{Mols } N_2}{82.4} \left| \frac{\text{Mols air}}{100} \right| \frac{\text{Cubic feet S. C.}}{359} \left| \frac{535}{492} \right. = 1{,}900 \text{ cu. ft.}$$

$$\left| \frac{100}{11.6} \right| \qquad \left| \frac{}{79} \right|$$

3. *Cubic feet kiln gas per gallon of oil.*

$$\frac{\text{Pounds oil}}{7.69} \left| \frac{\text{Atoms C}}{7.05} \right| \frac{100}{11.6} = 4.67 \text{ mols dry gas}$$

$$\left| \frac{}{100} \right|$$

7.69(5.40/100) = . . . 0.42 mols total moisture

Total gas per gallon = . . . 5.09 mols

5.09(359)(1,710/492) = 6,350 cu. ft. at 1,250°F.

4. *Dew point of the kiln gas.*

(0.42/5.09)29.92 = 2.46 in. = pressure of water vapor in gas.

The temperature at which water has this vapor pressure is 108°F., which is the dew point of the gas.

Illustration 9.—The average Orsat analysis of the gas from a furnace burning fuel oil is 12.9% CO_2, 3.8% O_2 and 83.3% N_2. Assuming the oil to consist only of hydrocarbons, calculate the weight per cent of carbon in the oil.

Basis.—100 mols dry gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	12.9	12.9	12.9
O_2	3.8	....	3.8
N_2	83.3		
Total	100.0	12.9	16.7 O_2 accounted for
83.3(21/79) =			22.15 O_2 from air
			5.45 O_2 disappearance

Net H_2 burnt = (5.45)2 = 10.9 mols = 22 lb.
C burnt (12.9)12 = ...155 lb.

Total combustible .....177 lb.

(155/177)100 = 87.6% C in oil.

Illustration 10.—A carbureted water gas has the following composition: C_2H_4, 16.6%; CH_4, 19.8%; H_2, 32.1%; CO, 26.1%; CO_2, 3.0%; and N_2, 2.4%. Upon combustion the flue gases are found to contain CO_2, 12.2%; CO, 0.4%; O_2, 4.0%; and N_2, 83.4%. From these two analyses, compute:

1. The cubic feet of air per cubic foot of gas fired, both measured at 70°F. and 28.5 in. pressure.

2. The cubic feet of flue gas per cubic foot of fuel burnt, the flue gas being at 680°F., and at a pressure lower by 0.95 in. of water than that of the water gas.

Solution.—There are two factors of interest in calculations concerning the combustion of gaseous fuels. In the first place, the analysis of the fuel is already on a molal basis. In the second place, the ratios, (cubic feet of air used)/(cubic feet of fuel used) and (mols of air used)/(mols of fuel used), are equal, as are also the ratios, (cubic feet of gas produced)/(cubic feet of fuel used) and (mols of gas produced)/(mols of fuel used), provided the volumes are measured under identical conditions of temperature and pressure. If at different temperatures or pressures, a

simple temperature or pressure ratio gives the cubic feet from the molal ratio.

Basis.—100 mols water gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
C_2H_4	16.6	33.2	33.2	
CH_4	19.8	19.8	39.6	
H_2	32.1	....	32.1	
CO	26.1	26.1	.....	13.0
CO_2	3.0	3.0	.....	3.0
N_2	2.4			
Total	100.0	82.1	104.9	16.0

Total H_2O from combustion = 104.9 mols.

Basis.—100 mols dry flue gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	12.2	12.2	12.2
CO	0.4	0.4	0.2
O_2	4.0	....	4.0
N_2	83.4		
Totals	100.0	12.6	16.4

1. *The cubic feet of air per cubic foot of gas fired.*

Basis.—1 mol fuel gas.

Mol water gas	Atoms C	N_2 from air	
1	82.1	83.4	100
	100	12.6	79

= 6.87 mols of air per mol of water gas

Note.—N_2 in water gas is neglected.

The air and water gas being at the same temperature and pressure, 6.87 is also the cubic feet of air per cubic foot of water gas.

2. *Cubic feet of flue gas per cubic foot of water gas.* From a carbon ratio:

$$(82.1/12.6) = 6.52 \text{ mols dry flue gas}$$
$$1.05 \text{ mols water vapor}$$
$$\text{Total flue gas} = 7.57 \text{ mols per mol fuel}$$

As the flue gas is at a higher temperature (680°F. = 1,140°R.[1]) than the fuel (70°F. = 530°R.), the cubic foot ratio is greater than 7.57 and is found by multiplying the molal ratio by the temperature ratio. Likewise, the flue gas is at a lower pressure, causing its volume to be greater also on this account. Since 0.95 in. of water equals 0.07 in. of Hg, the ratio to be used is $28.5/(28.5 - 0.07) = 28.5/28.43$. Hence,

$$7.57(1{,}140/530)(28.5/28.43) = 16.3 \text{ cu. ft. flue gas.}$$

Effect of Neglecting Nitrogen.—In the above calculations the nitrogen in the fuel was neglected and it will be shown that this method is justified, since by so doing the final results are not affected within the precision of the data.

For example, in Illustration 7, the coal contained 1.26% N_2, or $1.26/28 = 0.045$ mol per 100 lb. of coal. For the conditions of combustion there given, 35.10 mols N_2 were used per 100 lb. of coal. The effect of 0.045 mol N_2 in the coal on 35.10 mols in the flue gas is negligible.

Similarly, in the case of certain gaseous fuels, as, for example, the water gas given in Illustration 10, a small amount of nitrogen may be neglected in the calculations. The analysis of the water gas showed it to contain 2.4% N_2 by volume. On the basis of 1 mol of gas fired, the dry flue gas was computed as 6.52 mols. Of this, 83.4%, or 5.44 mols, is nitrogen. In this case, also, 0.024 mol from the fuel may perhaps be neglected in comparison, since it is less than half of 1%. However, the error is much larger than is usual for solid fuels.

With some fuels the nitrogen content is so high that the above method cannot be followed. This is well illustrated in the combustion of producer gas in the problem below, in which case the nitrogen from the fuel forms about 22% of the total present in the products of combustion.

Illustration 11.—A producer gas contains 9.2% CO_2, 0.4% C_2H_4, 20.9% CO, 15.6% H_2, 1.9% CH_4 and 52.0% N_2. When burnt, the products of combustion are found to contain 10.8% CO_2, 0.4% CO, 9.2% O_2 and 79.6% N_2. Compute:

1. The cubic feet of air used in the combustion of one cubic foot of producer gas, both being at the same temperature and pressure.

2. The per cent excess air used in combustion.

[1] °R. means degrees Rankine, *i.e.*, degrees Fahrenheit absolute.

3. The per cent of the nitrogen in the products of combustion which came from the producer gas.

Basis.—100 mols producer gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	9.2	9.2	....	9.2
C_2H_4	0.4	0.8	0.8	
CO	20.9	20.9	....	10.45
H_2	15.6	....	15.6	
CH_4	1.9	1.9	3.8	
N_2	52.0			
Total	100.0	32.8	20.2	19.65

Basis.—100 mols dry combustion gas.

Gas	Mols	Atoms C	Mols O_2	Mols N_2
CO_2	10.8	10.8	10.8	
CO	0.4	0.4	0.2	
O_2	9.2	....	9.2	
N_2	79.6	....	....	79.6
Total	100.0	11.2	20.2	79.6

The nitrogen in the combustion gas evidently comes from two sources, the producer gas and the air. On the other hand, the carbon in this gas was present originally in the producer gas only. From the analysis of the latter the nitrogen: carbon ratio in it (52.0/32.8) is obtained, and this ratio multiplied by the carbon in the combustion gas (11.2 atoms) gives immediately the quantity of nitrogen (17.75 mols) from the producer gas. Subtracting this quantity from the total nitrogen present leaves as a residue 61.85 mols of atmospheric nitrogen. The oxygen associated with the latter is 61.85(21/79) = 16.4 mols O_2 from the air. The excess oxygen (allowing for the 0.4 mol CO present) is 9.2 − 0.2 = 9.0 mols O_2 excess.

The principle employed in this step should be studied carefully, because, as will later appear, it is frequently helpful in simplifying computations. In burning a fuel rich in nitrogen, the nitrogen in the flue gas is not a direct measure of the air employed for combustion, because a part of it comes from the fuel. On the other hand, it is possible, as shown above, to earmark and set

aside the nitrogen from the fuel, the remainder coming from the air alone and being treated accordingly. The method of earmarking one or more portions of a constituent will be referred to repeatedly in later chapters.

1. *Cubic feet of air used per cubic foot of producer gas.*

Basis.—1 mol fuel.

Mols fuel	Atoms C	N_2 from air	
1	32.8	61.85	100
	100	11.2	79

$= 2.29$ mols air per mol producer gas

This is equal to the cubic feet of air per cubic foot of producer gas, provided both are at the same temperature and pressure.

2. *Per cent excess air.*

$$\frac{100(9.0)}{(16.4 - 9.0)} = 160.1\%.$$

3. *Per cent of nitrogen in the combustion gas which came from the producer gas.*

$$\frac{100(17.75)}{79.6} = 22.3\%.$$

If in the combustion of any solid or liquid fuel it seems desirable to allow for nitrogen in it, this may be done by the same method.

Effect of Neglecting Sulfur.—In all of the above problems the sulfur has been disregarded entirely. For example, in Illustration 8, the oil contained 1.63% S. This would be only 1.63/32 = 0.05 atom of S or mol of SO_2 per 100 lb. of oil as against 7.05 mols of CO_2 or CO from the same amount of fuel. Neglecting the sulfur affects the CO_2 less than 1%; considering the accuracy of its determination, the error is usually negligible. The same is, in general, true of coals which contain normal amounts of sulfur.

With some coals, however, this must not be done. For example, a Kansas coal contains 8.33% S and 65.02% C, giving per 100 lb. of coal, 8.33/32 = 0.26 atom of S or mol of SO_2 and 65.02/12 = 5.42 atoms of C or mols of CO_2. If the gas from a furnace burning this coal be collected over water in the gas-analysis apparatus, the SO_2 will be largely dissolved and the gas analyzed will be practically SO_2-free. Neglecting this SO_2 formation from a high-sulfur coal such as the above would introduce a serious error in any computation involving an oxygen balance.

Collection of the gas sample over mercury probably offers the best means for overcoming these difficulties. In that case both the SO_2 and the CO_2 are retained in the gaseous phase and they are determined together by absorption in caustic alkali. In the case of the coal cited above, if the combined percentages of these two gases were 15% of the total gas volume, this should be divided between the CO_2 and the SO_2 in the ratio of 5.42:0.26, giving 14.3% CO_2 and 0.7% SO_2 in the gas.

Nitrogen and sulfur in the fuel cannot be neglected in calculating the carbon in it by difference, as otherwise the per cent carbon so obtained will be too high by an amount corresponding to the sum of these two elements present. This is true even in cases in which in the flue-gas analysis from the same fuel these two elements may be neglected.

In general, a part of the sulfur remains in the ash and, where the sulfur content of the fuel is high, it may occasionally be necessary to allow for this. Stoichiometrically, such sulfur plays no part in combustion. Total sulfur less that in the ash may, therefore, be called "net" or combustible sulfur. Since oxygen in the coal is obtained by difference, in computing it only net sulfur should be used, since otherwise sulfur in the ash would be counted twice.[1] Furthermore, net sulfur requires oxygen to burn it. Whether this be assumed to come from the oxygen of the coal or from the air is stoichiometrically immaterial, but it is perhaps simpler to assume the former, thereby reducing the oxygen available to form combined water and correspondingly increasing the net hydrogen. The amount of oxygen to be deducted for the net sulfur depends on the extent to which the SO_2 is oxidized to SO_3. While this always occurs to some extent, it is usually allowable to neglect the oxidation beyond the SO_2 stage.[2]

Illustration 12.—A furnace uses a coal the ultimate analysis of which shows 57.22% C, 5.64% H, 1.41% N, 5.06% S and 14.67%

[1] However, as stated on p. 11, in the ultimate analysis correction for the sulfur in the ash is not usually made.

[2] In computing the oxygen in the so-called true coal substance by difference from 100, where sulfur exists in the coal as pyrites, neglecting any sulfur left in the ash, one subtracts not the total sulfur, but five-eighths of it. For combustion computations this is wrong; on the same assumptions one should subtract the whole of the sulfur. Obviously, however, the result will be unchanged by this allowance for pyritic sulfur if one will treat it in further computations as such, by the methods of Chap. V, but this greatly complicates computation.

ash. The combustible matter left in the ash from the furnace is negligible. The ash of this particular coal is found by analysis to contain 9.62% S. On the assumption that this furnace secures complete combustion, using 80% excess air, all the sulfur in the combustion gases appearing as SO_2, compute the Orsat analysis of the combustion gases, if the sample be collected through a tube filled with PbO_2 (which quantitatively removes SO_2). What is the per cent net hydrogen in this fuel? What would be the computed per cent net hydrogen if, as is normally the case, the sulfur in the ash were neglected?

Solution.—The sulfur determined by analysis is the total sulfur. Since part of it remains in the ash, part of it belongs there when arranging the results of the analysis. Taking a basis of 100 lb. of coal, this amount is 14.67(0.0962) = 1.41 lb., included in the ash as determined. The remainder of the sulfur, 5.06 − 1.41 = 3.65 lb., is the sulfur converted to SO_2, *i.e.*, the "net" sulfur. Arranging the analysis in tabular form, using the value 3.65 for sulfur, one obtains the oxygen by difference. From this total oxygen, there is deducted the oxygen equivalent to the sulfur, the remainder being oxygen equivalent to combined water.

Basis.—100 lb. coal.

	Pounds	Mols or atoms
C	57.22	4.77
H_2	5.64	2.79
N	1.41	
Net S	3.65	0.114
Ash	14.67	
O (by difference)	17.41	1.088
Total	100.00	

O = net S = 2(0.114) = 0.228 atom
Net O = 1.088 − 0.228 = 0.86 atom O as combined water
Net H_2 = 2.79 − 0.86 = 1.93 mols
Net H_2 = 1.93(2.02) = 3.88 lb., or 3.88%
O_2 for theoretical combustion = 4.77 + 1.93/2 = 5.74 mols
Excess O_2 = 0.80(5.74) = 4.59 mols
N_2 from air = (5.74 + 4.59)(79/21) = 38.9 mols

Flue gas (dry, SO_2-free) contains:

Gas	Mols	Per cent
CO_2	4.77	9.9
O_2	4.59	9.5
N_2	38.9	80.6
Total	48.26	100.0

If the sulfur in the ash be neglected, the following is obtained:

Basis.—100 lb. coal.

	Pounds	Mols or atoms
C	57.22	4.77
H_2	5.64	2.79
N_2	1.41	
S	5.06	0.158
Ash	14.67	
O (by difference)	16.00	1.00

$O \simeq S = 2(0.158) = 0.316$ atom
Net $O = 1.00 - 0.316 = 0.684$ atom O as combined water
Net $H_2 = 2.79 - 0.68 = 2.11$ mols
Net $H_2 = 2.11(2.02) = 4.26$ lb., or 4.26%

The error is about 10% of the net hydrogen.

In order to summarize the ideas presented, an example will be given in which a number of these factors are brought together in one problem. This makes the apparent complexity of the problem greater, but in reality the unit computations merely employ step by step the principles developed above.

Illustration 13.—The stack gas from a boiler furnace contains 10.8% CO_2, 0.2% CO, 9.0% O_2 and 80.0% N_2. These gases enter the stack at 760°F., at a draft of 0.5 in. of water; 1,200 lb. of coal are burnt per hour. The proximate analysis of the coal as fired is 1.44% moisture, 34.61% volatile matter, 57.77% fixed carbon and 6.18% ash, and the heating value is 14,350 B.t.u. per pound. An analysis for carbon and sulfur shows these to be 78.76% and 0.78% respectively. Furthermore, it is known that coal from the same field averages 1.3% N. The volatile matter of the refuse (dry) is 4% and the fixed carbon 21%. Air in the boiler room has a temperature of 74°F., and is 65% saturated with water vapor. The barometer is 29.7 in. Compute:

1. The per cent heat loss due to unburnt combustible.
2. The per cent heat loss due to CO in the stack gas.
3. The per cent of the heating value required to vaporize the total water vapor formed on combustion.
4. The per cent heat loss as sensible heat in the stack gas.
5. The per cent excess air used in the combustion.
6. The cubic feet of air used per minute for combustion.
7. The cubic feet of gas entering the stack per minute.

Solution.—It is obvious that the composition of the flue gas is determined not by total combustible fired, but only by combustible actually burnt. The data for securing the relation between combustible fired and burnt is found in the analyses of fuel and refuse. On the other hand, the analysis of the fuel is not complete and hence the relation between net hydrogen and carbon must be determined from the flue-gas analysis, this applying, however, only to combustible actually burnt. Therefore, in solving this problem the first step is to get the relation between combustible burnt and combustible fired from the analyses of fuel and refuse, next, to secure the relation between net hydrogen and carbon in combustile burnt from the flue-gas analysis and finally, by tying these two together, to compute the composition of the fuel. With the data thus organized and tabulated, solution of the various parts of the problem reduces itself to selecting and combining the specific quantities required in each case.

Basis.—100 lb. refuse.

	Pounds
Volatile matter	4
Fixed carbon	21
Ash	75
Total	100

$\therefore$ uncoked combustible matter $= 4(34.61 + 57.77)/34.61 = 10.7$ lb.
$\therefore$ C present as coke $= 21 + 4 - 10.7 = 14.3$ lb.

From fuel analyses:

$$\text{Per cent C in combustible matter} = \frac{78.76 \times 100}{34.61 + 57.77} = 85.3\%$$

$\therefore$ C present in uncoked combustible matter $= 0.853(10.7) = 9.1$ lb.
$\therefore$ total C present $= 14.3 + 9.1 = 23.4$ lb.

Basis.—100 mols dry stack gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	10.8	10.8	10.8
CO	0.2	0.2	0.1
O_2	9.0	....	9.0
N_2	80.0		
Total	100.0	11.0	19.9 O_2 accounted for
80.0(21/79) =			21.25 O_2 from air
O_2 unaccounted for by analysis =			1.35 O_2 disappearance

$\therefore$ net H_2 burnt to H_2O = 2(1.35) = 2.70 = H_2O from combustion
Pounds net H_2 burnt, 2.70(2.02) = 5.45
Pounds C burnt, 11.0(12) = 132
Net H_2 burnt: C burnt = 5.45: 132.

Basis.—100 lb. coal as fired.

	Pounds	
C, total =	78.76	
C in refuse, 6.18(23.4/75) =	1.93	
C in gas =	76.83	= 6.40 atoms.
Net H_2 in gas, (5.45/132)76.83 =	3.17	= 1.57 mols
C as uncoked coal in refuse, 6.18(9.1/75) =	0.75	
C corresponding to net H_2 in gas,[1] 78.76 − 0.75 =	78.01	
Net H_2 in refuse, (0.75/78.01)3.17 =	0.305	
Total net H_2 in coal, 3.17 + 0.30 =	3.47	

Coal Analysis.

C	78.76	
Net H_2	3.47	
S	0.78	
N	1.30	
Ash	6.18	
Moisture	1.44	= 0.08 mol
Total	91.93	
Combined H_2O	8.07	
Total	100.00	

Combined water in gas, 8.07(78.01/78.76) = 8.0 lb. = 0.44 mol
$\therefore$ total H_2O in gas from coal = 1.57 + 0.08 + 0.44 = 2.09 mols

[1] This is the total carbon in the coal from which came the net hydrogen in the gas.

The complete analyses of gas and fuel are now given. The general method of utilizing them is to employ a carbon ratio to give the relation between gas and fuel, and a nitrogen ratio to give that between dry gas and dry air. To complete the solution, it is necessary to determine the water in the flue gas. This water from a coal-fired furnace comes from four sources:

a. The water brought in with the air.

b. The moisture content of the coal.

c. The combined water in the coal (equivalent to the oxygen content of the fuel).

d. The water from the combustion of the net hydrogen present in the coal.

Item *a* is obtained through a nitrogen balance from the amount of air and its humidity. Item *b* comes from the proximate analysis of the coal. Item *c* is given by the ultimate analysis of the fuel, while item *d* is calculated from the net hydrogen in the fuel, in turn determined by the difference between total oxygen from the air and total oxygen in the flue gas. The last three come through a carbon balance.

1. *The per cent heat loss due to unburnt combustible.* As unburnt coal:

Basis.—1 lb. coal.

$$\frac{\text{Pounds ash}}{0.0618} \Big| \frac{\text{Pounds combustible in refuse}}{10.7} \Big| \frac{\text{Fraction loss}}{100} \Big| \frac{100}{\quad} = \frac{\quad}{75} \Big| \frac{\quad}{92.38} \Big| \frac{\quad}{\quad} = 0.95\%$$

As coke:

$$\frac{\text{Pounds ash}}{0.0618} \Big| \frac{\text{Pounds C}}{14.3} \Big| \frac{\text{C.h.u.}}{97,000} \Big| \frac{\text{B.t.u.}}{1.8} \Big| \frac{100}{\quad} = \frac{\quad}{75} \Big| \frac{\quad}{12} \Big| \frac{\quad}{\quad} \Big| \frac{\quad}{14,350} = 1.19\%$$

Total loss = 1.19 + 0.95 = 2.14%.

2. *The per cent heat loss due to CO in the stack gas.*

$$\frac{\text{Atoms C in gas}}{0.0640} \Big| \frac{\text{Mols CO}}{0.2} \Big| \frac{\text{C.h.u.}}{68,000} \Big| \frac{\text{B.t.u.}}{1.8} \Big| \frac{100}{\quad} = \frac{\quad}{11.0} \Big| \frac{\quad}{\quad} \Big| \frac{\quad}{\quad} \Big| \frac{\quad}{14,350} = 1.0\%$$

3. *The per cent of the heating value required to vaporize the total water vapor formed on combustion.*

$$\frac{\text{Mol } H_2O}{0.0209} \left| \frac{\text{Pounds}}{18} \right| \frac{\text{B.t.u.}}{1{,}050} \left| \frac{100}{14{,}350} \right. = 2.75\%$$

4. *The per cent heat loss as sensible heat in the stack gas.*

Basis.—100 mols dry stack gas.

Water vapor (from net hydrogen, combined water and moisture) from combustion of coal, $11.0(2.09/6.40) = 3.59$ mols.

Water vapor from air (vapor pressure H_2O at 74°F. = 0.84 in.; partial pressure at 65% saturation = 0.54 in.):

$$\frac{\text{Mols } N_2}{80.0} \left| \frac{\text{Mols dry air}}{79} \right| \frac{0.54}{(29.7 - 0.54)} = 1.88 \text{ mols.}$$

Total water vapor, $3.59 + 1.88 = 5.47 = 5.5$ mols approximately.

Gas	Mols	Heat content, B.t.u.		Difference = heat loss per mol	Total heat loss, B.t.u.
		At 760°F.	At 74°F.		
CO_2	10.8	7,250	370	6,880	74,400
CO, O_2, N_2	89.2	5,100	290	4,810	429,000
H_2O	5.5	6,100	350	5,750	31,600
Total	105.5	.....	...	.....	535,000

Basis.—1 lb. coal.

$$\frac{\text{Atoms C}}{0.0640} \left| \frac{\text{B.t.u. loss}}{535{,}000} \right| \frac{100}{14{,}350} = 21.7\%$$

5. *The per cent excess air used in combustion. Based on the substance burnt.*

$$\frac{(9.0 - 0.1)100}{21.25 - (9.0 - 0.1)} = 72\% \text{ excess air.}$$

Based on the coal fired.

Basis.—100 lb. coal.

$78.76/12 = 6.56$ O_2 required for C.
$(3.47/2.02)/2 = 0.86$ O_2 required for net H_2
7.42 O_2 required for combustion
$8.9(6.40/11.0) = 5.18$ O_2 used in excess
$(5.18/7.42)100 = 69.7\%$ excess air.

6. *The cubic feet of air used per minute for combustion.*

Pounds coal	Atoms C in gas	Mols N_2	Mols dry air	Mols humid air	Cubic feet S.C.	At 29.7 in.		
1200	6.40	80.0	100	29.7	359	29.92	534	= 4,710 cu. ft. air
60	100	11.0	79	(29.7 − 0.54)		29.7	492	

7. *Cubic feet of gas entering stack per minute.* A draft of 0.5 in. of water = (0.5/13.6) = 0.04 in. of Hg. The pressure of the stack gas is, therefore, 29.7 − 0.04 = 29.66 in. of Hg.

Pounds coal	Atoms C in gas	Mols wet gas	Cubic feet S. C.	At 29.66 in.		
1,200	6.40	105.5	359	29.92	1,200	= 11,000 cu. ft. gas
60	100	11.0		29.66	492	

PROBLEMS

1. Hydrogen-free carbon in the form of coke is burnt (*a*) with complete combustion using theoretical air, (*b*) with complete combustion using 50% excess air and (*c*) using 50% excess air but with 10% of the carbon burning to CO only. In each case calculate the gas analysis which will be found by testing the flue gases with an Orsat apparatus.

2. If dry hydrogen gas at atmospheric pressure is burnt completely in a furnace with 32% excess air, calculate the Orsat analysis of the flue gas from this furnace. *Ans.* 6% O_2, 94% N_2.

3. If moist hydrogen containing 4% of water by volume is burnt completely in a furnace with 32% excess air, calculate the Orsat analysis of the resulting flue gas. *Ans.* 6% O_2, 94% N_2.

4. If pure methane is burnt completely in a furnace with theoretical air, calculate the analysis of the resulting flue gas. *Ans.* 11.7% CO_2, 88.3% N_2.

5. Repeat the preceding problem on the assumption that 32% excess air is employed. *Ans.* 8.6% CO_2, 5.5% O_2, 85.9% N_2.

6. Calculate the flue-gas analysis obtained upon burning pure methane with 20% excess air on the assumption that 8% of its carbon content is burnt to monoxide rather than to dioxide. *Ans.* 8.74% CO_2, 0.76% CO, 4.2% O_2, 86.3% N_2.

7. A steel-annealing furnace burns a fuel oil, the composition of which can be represented as $(CH_2)_n$. It is planned to burn this fuel with 12% excess air. Assuming complete combustion, calculate the Orsat analysis of the flue gas. Repeat this problem on the assumption that 5% of the carbon in the fuel is burnt to CO only. *Ans.* (*a*) 13.3% CO_2, 2.4% O_2, 84.3% N_2; (*b*) 12.64% CO_2, 0.66% CO, 2.7% O_2, 84.0% N_2.

8. An annealing furnace uses a fuel oil containing 16.4% H and 83.6% C. It is proposed to fire this furnace with 25% excess air. Calculate the flue-gas analysis, assuming complete combustion. Repeat the calculation assuming that 5% of the total carbon is burnt to CO only. *Ans.* (*a*) 11.3% CO_2, 4.5% O_2, 84.2% N_2; (*b*) 10.7% CO_2, 0.55% CO, 4.75% O_2, 84.0% N_2.

9. A coke-fired furnace uses a fuel containing 81% C, 0.8% H and the rest ash. This furnace is designed to operate with 60% excess air. Calculate the flue-gas analysis, assuming complete combustion and repeat, assuming that 5% of the carbon is burnt to CO only. *Ans.* (*a*) 12.8% CO_2, 7.9% O_2, 79.3% N_2; (*b*) 12.1% CO_2, 0.6% CO, 8.2% O_2, 79.1% N_2.

10. A billet preheating furnace uses a coal containing 74% C, 4.8% H, 9.4% ash and negligible S and N. This furnace is to be fired with 50% excess air. Calculate the flue-gas analysis on the assumption of complete combustion and repeat on the assumption that 10% of the carbon burns to CO only. *Ans.* (*a*) 12.5% CO_2, 7.1% O_2, 80.4% N_2; (*b*) 11.25% CO_2, 1.25% CO, 7.7% O_2, 79.8% N_2.

11. In problems 4, 5 and 6 the flue gases go to the stack at 750°F., and 1 atm. The fuel gas is measured at 70°F. The air used for combustion is dry and at 1 atm. What is the volume of flue gas in cubic feet per 100 cu. ft. of fuel? What is the volume of air used, in cubic feet per 100 cu. ft. of fuel?

12. In problems 7 to 10 the flue gases go to the stack at 750°F., and 1 atm. The air used for combustion is at 70°F., and dry. What is the volume in cubic feet of stack gases per pound of fuel burnt? How many cubic feet of air per pound of fuel were used for combustion?

13. The flue gases from a furnace fired with a hydrogen-free coke contain 14.2% CO_2 and 6.7% O_2. These gases enter the stack at 740°F. The air used for combustion is substantially dry and enters the furnace at 70°F. Barometer = 760 mm.

(*a*) What is the volume in cubic feet of the flue gases leaving this furnace for each pound of carbon burnt? *Ans.* 514 cu. ft.

(*b*) What is the volume of air entering the furnace per pound of carbon burnt? *Ans.* 227 cu. ft.

(*c*) What percentage excess air is used in this furnace? *Ans.* 47.2%.

14. The flue gases from a furnace fired with hydrogen-free coke contain 13.9% CO_2, 1.0% CO and 6.4% O_2. These gases enter the stack at 740°F. The air used for combustion is substantially dry and enters the furnace at 70°F.

(*a*) What is the volume in cubic feet of the flue gases leaving this furnace for each pound of carbon burnt? *Ans.* 489 cu. ft.

(*b*) What is the volume of air in cubic feet entering the furnace per pound of carbon burnt? *Ans.* 215 cu. ft.

(*c*) What percentage excess air is used in this furnace? *Ans.* 39.6%.

15. The hydrogen gas obtained as a by-product in the electrolytic decomposition of salt to produce caustic and chlorine is burnt in a gas-fired furnace. The flue gases from this furnace are collected in a sampling device and analyzed in an Orsat. They are found to contain 5.4% O_2 and the rest N_2. The fuel enters the furnace dry, at 80°F., and 820 mm. absolute pressure. The barometer is 750 mm. The flue gases go to the stack at 650°F.

(*a*) If the flue gases from this furnace were cooled to 80°F., dried and measured at the same pressure as the original hydrogen, what volume of dry flue gases would be obtained per 100 cu. ft. of fuel fed to the furnace? *Ans.* 255 cu. ft.

(*b*) What is the actual volume of flue gas going to stack per 100 cu. ft. of fuel fed to the furnace? *Ans.* 794.7 cu. ft.

(*c*) What per cent excess air is used in burning this gas? *Ans.* 27.6%.

16. Methane is burnt in a furnace and the Orsat analysis of the flue gas shows 8.75% CO_2, 5.25% O_2 and 86% N_2. The fuel is dry and fed to the furnace at 60°F., and 1 atm. The stack gases are at 800°F.

(*a*) What is the volume of stack gases per 100 volumes of fuel?

(*b*) What is the per cent excess air?

(*c*) Check the flue-gas analysis against that of the fuel.

17. The flue gases from a calcining furnace contain 11.1% CO_2, 5.7% O_2, 0.8% CO, 6.3% H_2O and the rest N_2. These gases go to the regenerator at 1700°C., entering the regenerator at the rate of 22,000 cu. ft. per minute. In the regenerator they are cooled to 200°C. From the following formulas for the molal heat capacities of the components, compute the B.t.u. per hour which must be abstracted from these gases in the regenerator.

N_2, O_2, CO..... $MC_p = 6.50 + 0.0010T_k$

H_2O..... $MC_p = 8.81 - 0.0019T_k + 0.00000222T^2_k$

CO_2..... $MC_p = 7.0 + 0.0071T_k - 0.00000186T^2_k$

18. Recompute the preceding problem, using Figs. 1 and 2 instead of the formulas there given.

19. A coal contains 7% moisture, 22% volatile combustible matter, 63% fixed carbon and 8% ash and has a heating value of 14,900 B.t.u. per pound. The ash removed from a furnace using this coal contains 8% volatile combustible matter, 34% fixed carbon and 58% ash. Estimate the per cent of the heating value of this coal which is lost in this furnace as unburnt combustible in the ash. *Ans.* 5.5%.

20. Assuming that the nitrogen of problem 17 comes wholly from the air entering the furnace, that this furnace is continuous in operation and that 15% of the heat removed from the flue gases in the regenerator is lost by conduction and radiation through the regenerator walls, compute the temperature to which air is preheated in the regenerator.

21. Compute the theoretical flame temperature of carbon burning with air to CO_2 and to CO.

22. A boiler is fired with a coal containing 76% C and 8% ash, burnt under conditions such that elimination of combustible matter from the ash is complete. The air enters the furnace at 20°F. and substantially dry. The sulfur and nitrogen in the coal are negligible. The flue gases go to the stack at 1 atm. and 640°F. The average flue-gas analysis shows 12.6% CO_2, 6.2% O_2 and no CO. Calculate the following:

(*a*) The ratio by weight of net hydrogen to carbon in the coal and from this the per cent of net hydrogen in the coal.

(*b*) The per cent excess air used in the furnace.

(*c*) The complete analysis of the original fuel.

(*d*) The total volume of flue gases going to the stack for each pound of coal fired.

(*e*) The volume of air entering the furnace per pound of fuel fired.

23. A boiler is fired with a coal containing 76% C and 8% ash, burnt under conditions such that elimination of combustible matter from the

ash is complete. The air enters the furnace at 20°F., and substantially dry. The sulfur and nitrogen in the coal are negligible. The flue gases go to the stack at 1 atm. and 640°F. The average flue-gas analysis shows 12.6% CO_2, 6.2% O_2 and 1% CO. Calculate the following:

(*a*) The ratio by weight of net hydrogen to carbon in the coal and from this the per cent of net hydrogen in the coal.

(*b*) The per cent excess air used in the furnace.

(*c*) The complete analysis of the original fuel.

(*d*) The total volume of flue gases going to the stack for each pound of coal fired.

(*e*) The volume of air entering the furnace per pound of fuel fired.

24. Solve problem 22 on the assumption that the air enters 80% saturated at 90°F., at which temperature the partial pressure of water is 36 mm.

25. Repeat problem 24 on the assumption that in firing this coal it is necessary to wet it down with a hose in order to prevent dusting as the coal is introduced into the furnace, the water added in this way amounting to 12% of the coal as analyzed, the sample for analysis having been taken as the coal enters the boiler house.

26. A boiler is fired with a coal containing 69% C, 5% S, 11% ash and negligible nitrogen. The Orsat analysis of the flue gas gives 11.2% CO_2, 6.9% O_2 and 1.2% CO. The CO_2 thus reported, however, includes any SO_2 in the gas because that is also soluble in alkali. The air enters the grate dry at 40°F. and the stack gases are 700°F. The barometer is normal. Assuming the sulfur in the coal to be burnt to SO_2, the SO_3 formation being negligible, compute the following:

(*a*) Per cent excess air used in the furnace.

(*b*) Complete analysis of the original fuel.

(*c*) Total volume of flue gases going to the stack for each pound of coal fired.

(*d*) Volume of air entering the furnace for each pound of coal fired.

27. A boiler is fired with a coal containing 69% C, 5% S, 2% N and 11% ash under such conditions that elimination of combustible matter from the ash is complete. The flue gas is sampled through a tube filled with dry PbO_2 to absorb SO_2. Its analysis shows 11.6% CO_2, 0.9% CO and 7.8% O_2. The air enters the furnace 50% saturated at 75°F., at which temperature the vapor pressure of water is 22.2 mm. The stack temperature is 760°F. The barometer is 740 mm. On the assumption that the sulfur all goes into the gas as SO_2 compute:

(*a*) The per cent excess air used in the furnace.

(*b*) The complete analysis of the fuel.

(*c*) The per cent error introduced into items (*a*) and (*b*) by neglecting the nitrogen in the coal.

(*d*) The B.t.u. lost up the stack per pound of fuel fired due to (1) unburnt CO, (2) latent heat of water, (3) sensible heat.

28. A boiler is fired with a coal containing 78% C and 11% ash, burnt under conditions such that the dry ash removed from the furnace contains 23% of combustible matter, present as fuel which has been thoroughly coked but from which all the carbon has not been burnt out. The air enters the furnace at 22°F. and substantially dry. The sulfur and nitrogen

in the coal are negligible. The flue gases go to the stack at 1 atm. and 640°F. The average flue-gas analysis shows 13% CO_2, 6.8% O_2 and 1.1% CO. Calculate:

(*a*) The ratio by weight of net hydrogen to carbon in the coal and from this the per cent of net hydrogen in the coal.

(*b*) The per cent excess air used in the furnace. *Ans.* Based on fuel burnt, 41.3%; on fuel fired, 35.5%.

(*c*) The complete analysis of the original fuel. *Ans.* 2.31% total H, 8.70% O.

(*d*) The total volume of the gases going to the stack per pound of coal fired.

(*e*) The B.t.u. lost up the stack per pound of fuel fired as (1) unburnt CO, (2) latent heat of water, (3) sensible heat.

29. A furnace is fired with a fuel oil containing 83% C and is substantially free from sulfur and nitrogen. The air used for combustion enters at 85°F., and with a partial pressure of water vapor of 26 mm. The flue gas contains 10.5% CO_2, 0.6% CO and 6.0% O_2. The stack gases leave the furnace at a temperature of 840°F., and under a draft of 1.6 in. of water. The oil as fired has a heating value of 20,220 B.t.u. per pound. The barometer is 748 mm. Per pound of fuel fired, compute the following:

(*a*) Cubic feet of free air entering the furnace. *Ans.* 273.6.

(*b*) Cubic feet of stack gases leaving the furnace. *Ans.* 1,690.5.

(*c*) B.t.u. lost in the stack gases due to unburnt CO. *Ans.* 458.

(*d*) B.t.u. lost in the stack gases due to sensible heat. *Ans.* 4,030.

(*e*) B.t.u. lost in the stack gases due to failure to condense the water formed upon combustion of the hydrogen in the fuel. *Ans.* 1,267.

(*f*) B.t.u. recoverable from the stack gases by cooling them by means of a heat exchanger to 300°F. *Ans.* 2,920.

(*g*) B.t.u. otherwise lost which would be recoverable by reducing the excess air to 10%, on the assumption that the percentage of the total carbon burnt which goes to CO remains the same as at present. *Ans.* 667.

(*h*) Temperature to which the entering air would be preheated in such an exchanger if the wall and other losses (by conduction, radiation, etc.) amount to 22% of the heat given up by the stack gases in passing through the exchanger. *Ans.* 566°F.

CHAPTER III

GAS PRODUCERS

As with furnaces and kilns, more information as to the performance of a gas producer can be secured by analysis of the gas than from any other single source. A complete test on a producer set is time-consuming, and the equipment is usually so arranged as to make it difficult or impossible to secure all the data needed, particularly the volume of gas formed. This is hard to measure because of the large volume involved, the variations in rate of production and the expense and inconvenience of meters of sufficient size and precision to handle the gas. The quantity of fuel used can, however, be easily and accurately determined. If one knows its carbon content and that of the gas, a carbon balance, corrected for soot, tar and any unburnt combustible in the refuse, will immediately give the quantity of gas.

Estimation of the steam consumption and of the extent of its decomposition in the producer is also of great importance. This is likewise difficult to determine directly, but, allowing for water vapor in the air and for moisture and combined water in the fuel, it may readily be obtained from the gas analysis and its water content.

Gas-producer computations are unique in that the manufacture of producer gas represents the combination of primary combustion with water-gas formation. A large fraction of the volatile matter of the fuel remains in the gas as CO, hydrocarbons and hydrogen. Hydrogen and oxygen (the latter combined as CO or CO_2) are also introduced into the gas by decomposition of the steam injected or of some of the combined water in the fuel. As in combustion in furnaces, the gas analysis of itself can be made to yield important quantitative information as to these reactions.

Illustration 1.—The average analysis of a certain producer gas is:

	Per Cent
CO_2	9.84
O_2	0.04
C_2H_4	0.18
CO	18.28
H_2	12.90
CH_4	3.12
N_2	55.64
Total	100.00

What conclusions may be drawn from these figures alone?

Solution.—As in combustion calculations, the figures are first tabulated so that the quantities of the individual elements are shown, taking as a basis 100 mols of dry gas. Assuming all the nitrogen comes from the air used, the corresponding oxygen is next computed. This is less than the total oxygen present in the gas (note the difference from ordinary combustion calculations), the remainder of necessity being equivalent to water decomposed, since this is the only other possible source of oxygen. The mols of water decomposed and the hydrogen formed therefrom are obviously twice the corresponding mols of oxygen. The hydrogen from the steam is, in turn, less than the total present; the difference between the two must be the net hydrogen from the fuel. All these calculations are indicated in the following table:

Basis.—100 mols of dry producer gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	9.84	9.84	.....	9.84
O_2	0.04	.....	.....	0.04
C_2H_4	0.18	0.36	0.36	
CO	18.28	18.28	.....	9.14
H_2	12.90	.....	12.90	
CH_4	3.12	3.12	6.24	
N_2	55.64			
Total	100.00	31.60	19.50	19.02
O_2 from air, 55.64(21/79) =			.....	14.80
O_2 from decomposition of water =			.....	4.22
H_2 from decomposition of water, 4.22(2) =			8.44	
H_2 from net H_2 in fuel			11.06	

It will be noted that the oxygen in the gas comes from two separate sources, air and decomposition of water. By a nitrogen balance, that from the former source is earmarked and set aside, that from the latter being obtained by difference. This makes it possible to earmark similarly that fraction of the total hydrogen derived from water, since it must be equivalent to the oxygen from the same source. The remainder of the hydrogen must come from the fuel.

By multiplying the atoms of carbon by its atomic weight the pounds of carbon per 100 mols of dry gas are found and similarly the net hydrogen and the water decomposed.

Pounds C in gas, 31.60(12) =	379.2
Pounds net H_2 in gas, 11.06(2.02) =	22.3
Pounds H_2O decomposed, 8.44(18) =	151.8

From these figures several ratios can be obtained which can be used to give other data. For example, per pound of carbon gasified there are:

151.8/379.2 = 0.400 lb. H_2O decomposed
(100/379.2) 359 = 94.8 cu. ft. dry gas, S. C., produced and
(55.64/379.2)(100/79)359 = 66.8 cu. ft. dry air, S. C., used.

It is usual to assume that the water decomposed thus calculated is limited to that entering as steam with the air, but such probably is not the case. It is true that in an updraft producer the moisture of the coal is driven off and swept out of the producer at a temperature too low to react with carbon at an appreciable rate, but, on the other hand, that oxygen in the coal substance which is often described as "combined water" does not come off upon thermal decomposition solely as water, but partly as CO, CO_2 and perhaps to some degree as oxygen-containing organic compounds. The latter almost certainly decompose into simpler molecules before leaving the producer. Consideration will show, however, that in so far as oxygen of the fuel reacts thus directly to yield CO and CO_2, an *equivalent* amount of hydrogen must be liberated so that *stoichiometrically* the result is the same as though the "combined water" of the fuel had first been set free as such and had then reacted with carbon. The data throw no light on the mechanism of these reactions, but fortunately it is entirely immaterial in the overall performance of

the producer. Similarly, of the net hydrogen in the coal some may burn to water and some distill off as hydrocarbons, but the exact equivalent of all of it must appear in some form in the product. The computations correctly represent the overall result, though the reaction mechanism may differ from that assumed in making them.

In all updraft producers the thermal decomposition and distillation of the coal take place at high temperature in an atmosphere free of oxygen. In consequence, the cracking of the distillation products results in the formation of considerable quantities of tar and soot. Where the hot gas goes directly into a furnace beside the producer, substantially all of the tar is carried into the furnace, but where the gas is piped any considerable distance and cooled, the tar settles in the flues, separates out in the coolers, collects in the traps and develops a general nuisance. Because of these conditions it is impossible to determine tar formation with any precision in a test run of normal duration. It can, however, be measured satisfactorily over long time periods, and the evidence indicates that the tar formation per pound of coal gasified remains substantially constant for a given coal in a given equipment so long as operating conditions are not too widely varied. The most satisfactory method of allowing for tar is, therefore, to secure data on tar formation over long periods of time and to use these figures in computing the results of a test rather than using the data on the tar obtained during the test itself. Since under normal conditions a large fraction of the tar separates out emulsified with water, it is imperative to have an analysis of the water content of the tar.

To get carbon and hydrogen balances on the producer, one must have the ultimate analysis of the tar. On the other hand, while tar formation is in no wise negligible, it is always a minor factor compared with the total combustible in the fuel, so that no serious error is introduced if its composition is estimated, particularly since it is known to be rich in carbon. In the absence of direct analyses of the tar in question, the authors usually assume it to contain 90% carbon and the rest hydrogen, although it is well recognized that it does carry some oxygen, nitrogen and sulfur.

Illustration 2.—The following data were obtained from a test on a Morgan gas producer. The feed was automatic, insuring uniform rate of fuel supply and eliminating any serious variations in rate of gas production. Using the same kind of coal

under similar conditions of operation over long periods of time, it has been found that the weight of dry tar produced is 3.9% of the weight of the coal fired. It is desired to determine the gas production, the steam decomposition and a heat balance on the producer itself.

ABSTRACT OF TEST SHEET

			Per Cent
Duration of run, hours	2.33	Combustible in refuse	9.99
Steam, pounds per hour	338	Coal analysis, wet basis:	
Steam pressure, pounds gage	15	Moisture	1.06
Coal, pounds per hour	866	C	69.40
Temperature of air, degrees Fahrenheit:		H	4.76
Dry bulb	65.5	S	1.48
Wet bulb	59.4	N	1.48
Barometer, inches of Hg	29.43	O	9.18
Temperature of exit gas	1305°F.	Ash	12.64
Average gas analysis, per cent by volume:		Heating value, B.t.u. per pound, dry	12,520
CO_2	7.23		
$Ill(C_2H_4)$	0.58		
O_2	0.38		
CO	20.76		
H_2	11.36		
CH_4	2.98		
N_2	56.71		

Determination of the water content of the gas was made in the following manner: A sample was drawn through a steam-jacketed filter of glass wool to remove tar and dust, and thence through an absorption bulb containing P_2O_5. In this manner 14.40 l. of the dried gas were collected at 32.0°C., and at 759 mm. pressure. The increase in the weight of the bulb was 0.8451 g.

Solution.—The coal and gas analyses are tabulated and, by using the information regarding the refuse and tar, the distribution of carbon and hydrogen is shown.

Basis.—100 lb. of coal as fired.

	Pounds	Mols or atoms
Moisture	1.06	0.06
C	69.40	5.78
H_2	4.76	2.36
S	1.48	
N_2	1.48	
O_2	9.18	0.29
Ash	12.64	
Net H_2, 2.36 − 2(0.29) =	....	1.78
Combined water, 2(0.29) =	....	0.58
C in refuse, 12.64(9.99/90.01) =	1.40	0.12
C in tar, 3.9(0.9) =	3.51	0.29
C in gas, 5.78 − 0.12 − 0.29 =	....	5.37
Net H_2 in tar, 3.9(0.10) =	0.39	0.19
Net H_2 in gas, 1.78 − 0.19 =	....	1.59

Basis.—100 mols of dry gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	7.23	7.23	.....	7.23
Ill. (C_2H_4)	0.58	1.16	1.16	
O_2	0.38	.....	.....	0.38
CO	20.76	20.76	.....	10.38
H_2	11.36	.....	11.36	
CH_4	2.98	2.98	5.96	
N_2	56.71			
Total	100.00	32.13	18.48	17.99

These two tabulated analyses of the coal and gas show, each on its own basis, how much carbon is present in the gas. Using the amount of coal fired as given in the table of test data, the gas production can be estimated directly by a carbon balance.

$$\frac{\text{Pounds coal per hour}}{\text{866}} \times \frac{\text{Atoms C in gas}}{\text{5.37}} \times \frac{\text{Mols dry gas}}{\text{100}} \times \frac{359}{100} \times \frac{100}{32.13} = 52{,}000 \text{ cu. ft. S. C. per hour}$$

A diagrammatic representation of this problem is seen in Fig. 3.

A virtually independent check may be had on this figure by using a hydrogen balance. Hydrogen occurs in so many places that it is best to tabulate the separate items.

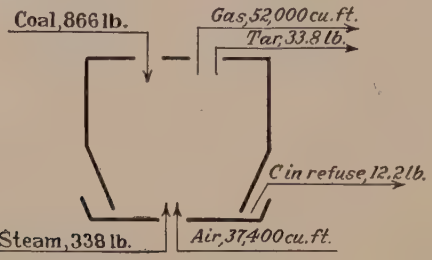


FIG. 3.—Material balance on gas producer. *Basis.*—1 hr.[1]

Hydrogen Input.—Basis.—1 hr.

a. From the coal.

Moisture + combined water + net H_2 = 0.06 + 0.58 + 1.59 = 2.23 mols per 100 lb. coal fired.

$$(2.23/100)866 = 19.3 \text{ mols per hour.}$$

b. From the steam.

$$338/18 = 18.78 \text{ mols per hour.}$$

c. From the air. This is obtained through the nitrogen in the producer gas, from which the air used can be computed. Let the quantity of dry producer gas be x mols per hour. From the wet- and dry-bulb temperatures of the air, the humidity is found to be 70%.[2] The vapor pressure of water at 65.5°F. is 0.63 in. This gives as the partial pressure of the water 0.70(0.63) = 0.44 in. of Hg, and as the pressure of the dry air 29.43 − 0.44 = 29.0 in. Thus the hydrogen brought in by the air as water vapor is

$$\frac{\text{Mols of producer gas } x}{\text{Mols } N_2} \Big| \frac{56.71}{100} \Big| \frac{\text{Mols dry air}}{100} \Big| \frac{79}{0.44} \Big| \frac{0.44}{29.0} = 0.0109x \text{ mol } H_2O \text{ vapor}$$

Hydrogen Output.—a. As water vapor in gas. The figures show that for every 14.40 l. of dry gas at 32.0°C. and 759 mm., there are 0.8451 g. of water vapor. This is equivalent to

[1] In the diagrams used to illustrate problems figures in Roman Type (*e.g.*, Coal, 866 lb.) refer to data given in the problem while those in Italics (*e.g.*, *Gas, 52,000 cu. ft.*) refer to calculated values.

[2] See any standard humidity tables.

Liters dry gas	At 0°C.	At S. C.	
14.40	273	759	
	305	760	22.4

= 0.575 g. mol dry gas

0.8451/18 = 0.047 g. mol water.

This is 0.047/0.575 = 0.0817 g. mol of water per g. mol of dry gas. This number is, of course, identical with the ratio of pound mols of water per pound mol of dry gas. Therefore, the hydrogen output in this form is $0.0817x$.

b. As H_2 in gas, $0.1848x$ mol.

The hydrogen balance is obtained by equating the input and output as calculated above.

$$19.3 + 18.78 + 0.0109x = 0.0817x + 0.1848x$$

This gives $x = 149.0$ or $149.0(359) = 53{,}500$ cu. ft. S. C., per hour.

The good agreement of this figure with that obtained from a carbon balance (52,000 cu. ft.) furnishes a check on the dependability of the data and the accuracy of the assumptions.

Steam Decomposition.—This also may be calculated by either the carbon or the hydrogen balance. The steam actually used is 18.78 mols per hour. The steam decomposed is equal to the number of mols of hydrogen in the gas corrected for the net hydrogen in the coal.

a. By carbon balance.

Pounds coal	Atoms C in gas	
866	5.37	18.48
	100	32.13

= 26.70 mols H_2 in gas

866(1.59/100) = 13.77 mols net H_2 from coal

12.93 mols H_2 from steam

(12.93/18.78)100 = 69% decomposed.

b. By hydrogen balance.

149(18.48/100) = 27.60 mols H_2 in gas

13.77 mols net H_2 from coal

13.83 mols H_2 from steam

(13.83/18.78)100 = 74% decomposed.

Heat Balance.—The temperature of the surroundings (65.5°F.) will be taken as the reference point for all items of heat input and output, all final results being reported on an hourly basis.

Heat Input.—a. Coal. The heating value is given for dry coal; hence it must be multiplied by the pounds of dry coal used: 866(0.9894)(12,520) = 10,720,000 B.t.u.

b. Steam. Fifteen-pounds gage pressure corresponds to 15(29.92/14.7) + 29.43 = 59.96 in. of Hg. To have this pressure, the steam (assumed saturated) must have a temperature of 249°F. Thus the heat content of the steam above 65.5°F. is (338/18)(1,780 − 280) = 28,200 B.t.u., this being the product of the mols of steam and the difference in molal heat content (Fig. 1, p. 5) between the two temperatures in question.[1]

The total heat input = 10,720,000 + 28,200 = 10,750,000 B.t.u.

Heat Output.—a. Heat required to vaporize water formed on combustion. The amount of water is equal to the total number of mols of hydrogen[2] plus the number of mols of moisture, 2.36 and 0.06 respectively, per 100 lb. of coal. The heat of vaporization of water at 65.5°F. is 1,068 B.t.u. per pound. The corresponding amount of heat is

Pounds coal	Mols H_2O	Pounds H_2O		
866	2.42	18	1,068	= 403,000 B.t.u.
	100			

[1] This use of the heat chart is not strictly correct, since the chart applies only to low-pressure steam (below atmospheric). The steam tables should be used. The error is negligible, however, especially since this term is small compared with the heating value of the coal.

[2] The hydrogen is included because the heat of combustion of the coal includes the heat of condensation of the water formed therefrom. It would be more logical to use the lower heating value of the coal, but this is seldom quoted because it requires a knowledge of the hydrogen in the coal, which must be determined independently of the calorimetric test.

b. Sensible heat in gas.

Basis.—1 mol dry gas.

Gas	Mols	Heat content, B.t.u.		Difference, B.t.u.	Product, B.t.u.
		At 1305°F.	At 65.5°F.		
CO_2	0.0723	13,800	300	13,500	976
O_2	0.0038				
CO	0.2076	9,200	230	8,970	8,002
H_2	0.1136				
N_2	0.5671				
CH_4	0.0298	.....	...	.....	472[1]
Ill	0.0058				
H_2O	0.0817	11,200	280	10,920	883
Total	1.0817	.....	...	.....	10,333

[1] This item is calculated from the equation for the molal heat capacity of methane, $7.5 + 0.005T$, by inserting for T its average value in °R $(1,305 + 66.5)/2 + 460 = 1,145$, remembering that the constant 0.005 is divided by 1.8 when T is in °R. This gives as the average molal heat capacity $7.5 + (0.005/1.8)(1,145) = 10.68$. The quantity of illuminants is small and is included with the methane, giving $(0.0298 + 0.0058)(10.68)(1,305 - 65.5) = 472$ B.t.u. absorbed in heating up these gases.

The heat retained by the hot gases is

Pounds coal	Atoms C in gas	Mols dry gas		
866	5.37	100	10,333	= 1,498,000 B.t.u.
	100	32.13		

c. Heat of combustion of the gas.

Basis.—1 mol of dry gas.

Gas	Mols	Higher heating value, C.h.u.	Product, C.h.u.
Ill. (C_2H_4)	0.0058	336,000	1,950
CO	0.2076	68,000	14,100
H_2	0.1136	68,300	7,750
CH_4	0.0298	212,000	6,320
Higher heating value, per mol	.....	.....	30,120

Pounds coal	Atoms C in gas	Mols dry gas	C.h.u.		
866	5.37	100	30,120	1.8	= 7,850,000 B.t.u.
	100	32.13			

d. Heat in tar. Assume the heat of combustion is equal to that of the component elements.

	B.t.u.
866(0.039)(0.10/2.02)(68,300)(1.8) =	207,000
866(0.039)(0.90/12)(97,000)(1.8) =	442,000
	649,000
Sensible heat:	
866(0.039)(1,305 − 65.5)(0.5)[1] =	21,000
Total heat in tar	670,000

[1] Specific heat of tar assumed equal to 0.5.

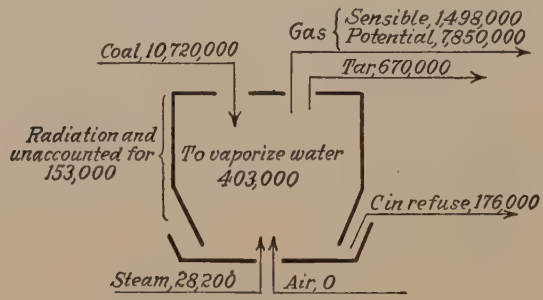


FIG. 4.—Heat balance on gas producer, figures represent B.t.u. *Basis.*—1 hr.

e. Heat of combustion of carbon in refuse.

Pounds coal	Pounds C	Atoms C	C.h.u.		
866	1.40		97,000	1.8	= 176,000 B.t.u.
	100	12			

The heat balance may now be written (See also Fig. 4.):

Heat input:

	B.t.u.
a. Coal	10,720,000
b. Steam	28,000
	10,750,000

Heat output:

a. Heat of vaporization of water of combustion	403,000
b. Sensible heat of hot gases	1,498,000
c. Heat of combustion of gases	7,850,000
d. Total heat in tar	670,000
e. Heat of combustion of C in refuse	176,000
f. Radiation and unaccounted-for losses	153,000
	10,750,000

PROBLEMS

1. A gas producer yields a gas containing 8% CO_2, 16.3% H_2, 20.6% CO, 1% CH_4 and 54.1% N_2. The coal fired contains 70% C, 3.5% moisture, 7.5% ash and negligible N and S. Tar formation can be neglected. Calculate:

(*a*) Cubic feet of gas produced (dry, S. C.) per pound of coal fired. *Ans.* 70.7.

(*b*) Cubic feet of air used (dry, S. C.) per pound of coal fired. *Ans.* 48.4.

(*c*) Pounds of steam decomposed per pound of coal fired. *Ans.* 0.278.

(*d*) Ultimate analysis of the fuel. *Ans.* 6.22% H, 16.28% O.

(*e*) Pounds of steam decomposed per pound of fuel fired, in excess of that brought in by the fuel itself. *Ans.* 0.095.

2. The coal of the preceding problem has a heating value of 12,500 B.t.u. per pound. The air enters the producer at 70°F., with a pressure of 18 mm. of water vapor. The barometer is 748 mm. The gas leaves the producer at 600°C., and its dew point is 120°F.

(*a*) What per cent of the heating value of the fuel appears as available heat of combustion in the gas, if the products of its combustion are cooled to room temperature? *Ans.* 77.4%.

(*b*) Per pound of fuel fired, how many B.t.u. are supplied to the producer as steam (feed-water temperature = 70°F.). Assume steam dry and saturated at barometric pressure. *Ans.* 562.

(*c*) What per cent of the steam supplied is decomposed in the producer, assuming all the water in the fuel to be driven off as such, and that the moisture in the entering air is decomposed in the same proportion as the steam? *Ans.* 49.3%.

3. The gases from a gas producer average 13.0% CO_2, 16.2% CO, 3.2% CH_4, 23% H_2 and 44.6% N_2. The coal fired contains 68% C, 4% moisture, 9% ash, 1.5% N and 1.2% S. The gas leaving the producer contains a suspension of tar, which is scrubbed out afterwards. Records over a long period indicate a tar formation of 180 lb. per ton of fuel fired. The tar analysis is 90% C and 10%H. The coal fired has a heating value of 12,980 B.t.u. per pound. The air enters at 75°F., and with a partial pressure of 12 mm. water vapor. The producer gas leaves at 550°C., the partial pressure of water vapor in it being 145 mm. The barometer is 750 mm. The gas as analyzed was sampled through PbO_2. Assume all sulfur went into the gas as SO_2. Calculate:

(*a*) Cubic feet of gas produced (dry, S. C.) per pound of coal fired. *Ans.* 55.4%.

(*b*) Per cent of steam supplied decomposed in the producer. *Ans.* 50.1%.

(*c*) Per cent of the heating value of the fuel appearing as sensible heat in the producer gas. *Ans.* 11.0%.

(*d*) Per cent of the heating value of the fuel lost in the tar, assuming the heating value of tar equal to that of its components. *Ans.* 13.3%.

CHAPTER IV

SULFUR COMPOUNDS

The sulfur used in industry is derived either from the element itself or from some sulfide ore, such as pyrites. Before conversion into other compounds, these are generally burnt to give SO_2. The operations are similar to the combustion of carbon compounds discussed in Chap. II, although special furnaces have to be employed.

Combustion of Sulfur.—While the main product of the primary combustion of sulfur is the dioxide, it is apparently impossible to avoid the formation of some trioxide. Normally, from 2 to 10% of the sulfur burnt is oxidized to the hexavalent state.[1] The vapor pressure of SO_3 is too great to allow it to condense as such at atmospheric pressure and temperature when formed by atmospheric combustion,[2] but when combined with water to form H_2SO_4 its condensation is quantitative. Since the usual gas analysis is carried out with saturated gas, the SO_3 is removed from the gas as H_2SO_4 before analysis starts. Hence, as in the analysis of combustion gases, water vapor is eliminated from the result, so in the analysis of sulfurous gases, any SO_3 formed does not appear. As in the former case, however, the water formed by oxidation of hydrogen can be determined by the oxygen disappearance, so too, in this case, the SO_3 can be computed in the same way. In both cases, this is possible because the oxygen supply is determined by the nitrogen in the gas, since all the oxygen comes in as air with a fixed $O_2:N_2$ ratio, and because all other products of oxidation appear in the gas analysis. Hence the oxidation product which disappears can be determined by difference.

[1] In the manufacture of bisulfites it is important to keep this percentage low, while in a sulfuric acid plant it may well be high.

[2] Were all the oxygen of air consumed to form SO_3, there would be two-thirds of 21, or 14, mols of SO_3 which, with the 79 mols of N_2, would give 15% SO_3. At a total pressure of 1 atm., the maximum possible partial pressure of SO_3 formed by atmospheric combustion of sulfur is, therefore, 0.15 atm., or 114 mm.

Assume that 10 atoms of S are burnt with 100 mols of air and that 90% of the S goes to SO_2 and the rest to SO_3. Since the reactions involved are $S + O_2 = SO_2$ and $2S + 3O_2 = 2SO_3$, it is obvious that 9 mols O_2 are consumed to form 9 mols of SO_2 and 1.5 mols O_2 to yield 1 mol SO_3. The remaining O_2 is, therefore, 21.0 − 10.5, or 10.5 mols. Since the SO_3 is condensed prior to analysis, the residual gas consists of 9 mols SO_2, 10.5 mols O_2 and 79 mols N_2, or a total of 98.5 mols. Hence the gas analysis shows 9.14% SO_2, 10.66% O_2 and 80.2% N_2.

In practice, the gas analysis is determined experimentally and from this the per cent of sulfur burnt to SO_3 may be computed. The preceding computation must, therefore, be reversed. Assuming the same analysis, the method is as follows:

Basis.—100 mols gas as analyzed.

Gas	Mols	Mols O_2
SO_2	9.14	9.14
O_2	10.66	10.66
N_2	80.2	
		19.80 = O_2 accounted for
80.2(21/79) =		21.32 = total O_2 from air
		1.52 = O_2 to SO_3 or 1.01 mols SO_3

Total S burnt = 9.14 + 1.01 = 10.15
Per cent of S as trioxide = (1.01/10.15)100 = 9.95%

The failure to check perfectly is due to the fact that the estimation of the SO_3 depends upon a small difference between relatively large quantities, and the cumulative error due to rounding off the second decimal place throws out the result. Careful gas analyses are essential if dependence is to be had upon the results, but the percentage error is serious only when the fraction of sulfur going to SO_3 is small.

In the important case of the use of SO_2 analyses of this type to determine SO_3 formation in individual units of a sulfuric acid plant, a valuable check is secured upon the results by using sulfur disappearance and oxygen decrease independently in the computations. They should be in the ratio $\frac{1}{2}O_2$:1S, and divergence from this ratio is an indication of error. Thus, the average composition of the gas entering a contact unit over a 12-hr. test period is found by analysis to be 7.2% SO_2, 13.2% O_2 and 79.6%

N_2 and leaving the unit 2.8% SO_2, 11.7% O_2 and 85.5% N_2. Of the SO_2 entering this unit, what per cent is oxidized to SO_3 in it?

Since the nitrogen goes through this operation unchanged, it should be used as the basis of the computation. The following tabulation is self-explanatory:

Basis.—100 mols N_2.

Gas	Mols in entering gas	Mols in exit gas	Decrease	Equivalent SO_3
SO_2	9.05	3.28	5.77	5.77
O_2	16.58	13.69	2.89	5.78

Hence, of the entering 9.05 mols of SO_2, (5.77/9.05)100 = 63.8% is oxidized to SO_3. Furthermore, the ratio of SO_2 decrease to oxygen decrease checks within 0.2%, giving independent confirmation of the dependability of the data.

When this method of testing and control is applied to chambers, the nitrogen oxides must be eliminated. This is easily done by collecting the gas samples through bubblers containing H_2SO_4 to absorb these oxides. Prior to taking the sample itself, enough gas should be drawn through the absorption train to saturate the absorbing acid with SO_2 at its partial pressure in the gas, in order to avoid loss of SO_2 before analysis. This is easily done and, at the same time, an average sample assured by drawing continuously an excess of gas through the absorbers by means of an aspirator and withdrawing only a fraction of this washed gas for analysis. The excess may be returned to the chamber, but at a point sufficiently removed so as not to contaminate the sample. The decrease in the ratio of SO_2:N_2 may then be taken as a quantitative measure of the acid formation between the sampling points. The oxygen decrease should not, however, check this unless the O_2:N_2 ratio in the eliminated nitrogen oxides as dissolved in the absorbing acid is the same at each sampling point, but since the amount of these oxides is not excessive and the ratio does not vary greatly, the error is usually negligible. This statement does not apply if the computation is carried back to the original air, since the nitrogen oxides as absorbed in H_2SO_4 do not normally have the same O_2:N_2 ratio

as the materials added to make up nitrogen losses. Errors due to N_2O formation and to any possible reduction of active nitrogen to the element are also usually negligible.

Combustion of Pyrites.—In the production of SO_2 by burning pyrites, oxygen disappears from the gas due not only to any SO_3 formation which may occur but also to the oxygen consumption necessary to give Fe_2O_3, which is a product of the combustion. In so far as the cinder is completely roasted to trivalent iron, this can be allowed for quantitatively by the relationships implied in the reactions:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 = 2Fe_2O_3 + 8SO_3.$$

Unburnt sulfide and lower oxides of iron can be determined by analysis of a representative sample of the cinder and allowed for. From a furnace well designed and operated, however, they should be small in amount. Allowance for sulfides of other metals can be based on the analysis of the pyrites. While the cinder usually holds relatively large quantities of sulfur, it should be in the form of adsorbed SO_3 (*i.e.*, basic sulfate). Since this is stoichiometrically equivalent to direct addition of SO_3 to the cinder, it does not affect the gas analyses or their quantitative interpretation, except that such SO_3 does not leave the furnace in the gas, and hence, to compute the SO_3 in the burner gas, this adsorbed SO_3 in the cinder must be subtracted from the total formed in the furnace, as indicated by the burner-gas analysis.

Thus, with 6.2% SO_2 and 12.1% O_2 in the average burner gas from a well-roasted pyrites, what percentage of the sulfur is exidized to SO_3 in the burner? From the preceding equations, on the basis of 100 mols of gas as analyzed, the oxygen consumed to form SO_2 is evidently 11/8 of 6.2, or 8.53 mols. Since the N_2 is 81.7, the O_2 from the air is 21.72 mols. Hence, O_2 unaccounted for is $21.72 - 12.1 - 8.53 = 1.09$, which is equivalent to 8/15 of $1.09 = 0.58$ mol SO_3. Hence, the total sulfur burnt is $6.2 + 0.58 = 6.78$ mols and the per cent oxidized to SO_3 is $100(0.58/6.78) = 8.6\%$. An analysis of the cinder would make it possible to tell how much of this left the burner in the gases.

Each of these steps in computation is simple. Difficulty arises solely from the fact that in plant problems it is usually necessary to deal with an interrelated series of such steps, and the mere amount of numerical work is sometimes confusing. The

following illustrations are intended to show the method of attack of the larger problems, but the elements involved remain unchanged.

Illustration 1.—A plant burns sulfur which is 99.4% pure at the rate of 680 lb. per hour. The average air temperature is 60°F. The gases emerge from the burner at 760°C., and are found to contain 17.4% SO_2 and 2.7% O_2 when analyzed[1] in the usual way. The gases then pass to a cooler, which reduces their temperature to 70°F. by means of water which rises from 58 to 90°F. Calculate:

1. The per cent of the sulfur burnt forming SO_3.
2. The amount of SO_2 leaving the burner in pounds per hour.
3. The air consumption in cubic feet per minute.
4. The volume of gas leaving the burner and the cooler in cubic feet per minute.
5. The heat dissipated from the burner in B.t.u. per hour.
6. The water used in the cooler in gallons per hour.

Solution.

Basis.—100 mols of gas as analyzed.

Gas	Mols	Mols O_2	
SO_2	17.4	17.4	
O_2	2.7	2.7	
N_2	79.9		
	100.0	20.1	= O_2 accounted for
79.9(21/79) =		21.21	= O_2 from air
		1.11	= O_2 disappearance

$\therefore$ S to SO_3 = (2/3)1.11 = 0.74 atom S = 0.74 mol SO_3

1. Since for every 17.4 mols of SO_2 produced, 0.74 mol of SO_3 is formed, 100(0.74)/(17.4 + 0.74) = 4.1% of the S burnt goes to SO_3, and 95.9% forms SO_2.

In order to secure the other information required, it is convenient to adopt the time bases indicated in the questions themselves.

[1] Mercury must be used on account of the marked solubility of SO_2 in water, but a single drop of water is kept above the mercury to saturate the gas.

2. *Basis.*—1 hr. of operation.

Pounds S burnt	Pounds pure S	Atoms S	Mols SO_2		
680	0.994		0.959	64.1	= 1,293 lb. SO_2 per hour
		32.1			

3. *Basis.*—1 min. Assume dry air and normal barometer.

Pounds SO_2	Mols SO_2	Mols N_2	Mols air	Cubic feet at S. C.		
1,293		79.9	100	359	520	= 743 cu. ft. air per minute
60	64.1	17.4	79		492	

The results of these calculations are shown in Fig. 5.

4. *Basis.*—1 min.

Pounds SO_2	Mols SO_2	Mols gas, including SO_3	Cubic feet at S. C.		
1,293		100.74	359	273 + 760	= 2,645 cu. ft. per minute leaving burner
60	64.1	17.4		273	

The volume of the gas leaving the cooler is found by correcting that leaving the burner for the temperature drop from 760°C. (1033°K.) to 70°F. (530°R.).

Cubic feet at 760°C.	At 0°C., or 32°F.		
2,645	273	530	= 753 cu. ft.
	1,033	492	

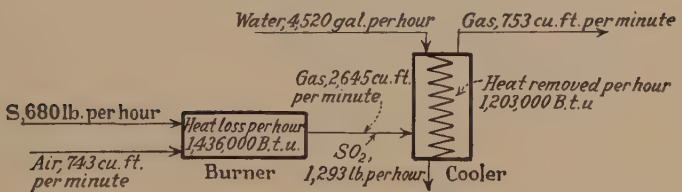

Water, 4,520 gal. per hour
Gas, 753 cu. ft. per minute
Gas, 2,645 cu. ft. per minute
Heat removed per hour 1,203,000 B.t.u
S, 680 lb. per hour
Heat loss per hour 1,436,000 B.t.u
Air, 743 cu. ft. per minute
SO_2, 1,293 lb. per hour
Burner
Cooler

FIG. 5.—Combustion of sulfur.

5. *Basis.*—100 mols gas as analyzed = 100.74 mols total gas (including SO_3).

The heats of reaction may be taken from the data of Berthelot, in Landolt-Börnstein, as $S + O_2 = SO_2 + 69{,}300$ cal. and $S + 1.5O_2 = SO_3 + 91{,}900$ cal. The heat evolved is, therefore,

17.4(69,300) + 0.74(91,900) = 1,273,000 C.h.u. = 2,290,000 B.t.u. The heat carried out by each gas is its number of mols times its total heat at 760°C. (1400°F.) less its total heat at 60°F., these values being read from Fig. 2 (p. 6), the total heat for SO_2 being the same as for CO_2. The total heat of SO_3 is not available, but it can be shown that its molal heat capacity is approximately 14 over the temperature range in question.

Heat Content of Gas Leaving Burner

Gas	Mols	Total heat, B.t.u.		Difference, B.t.u.	Product (= mols × difference), B.t.u.
		At 1400°F.	At 60°F.		
SO_2.....	17.4	14,800	250	14,550	253,000
SO_3.....	0.74	.....	...	14(1,340)	14,000
N_2, O_2.....	82.6	9,660	190	9,470	783,000
Total heat remaining in gases.....					1,050,000

The heat dissipated in the burners is that evolved (2,290,000 B.t.u.) less that carried out by the gases (1,050,000 B.t.u.) = 1,240,000 B.t.u. per 100 mols of gas as analyzed, or per 17.4 + 0.74 = 18.14 atoms of S burnt. Since the sulfur burnt per hour is 680 × 0.994/32.1 = 21.0 atoms, the heat dissipated per hour is (21.0/18.14)1,240,000 = 1,436,000 B.t.u. per hour.

6. *Basis.*—100 mols of gas as analyzed.

Heat Content of Gases between 1400 and 70°F.

Gas	Mols	Total heat, B.t.u.		Difference, B.t.u.	Product (= mols × difference), B.t.u.
		At 1400°F.	At 70°F.		
SO_2.....	17.4	14,800	340	14,460	250,000
SO_3.....	0.74	.....	...	14(1,330)	14,000
N_2, O_2...	82.6	9,660	260	9,400	776,000
Total heat removed from gases.....					1,040,000

As before, this quantity is on a basis of 18.14 atoms of S burnt. Converting to an hourly basis, which corresponds to 21.0 atoms of S, gives 1,040,000(21.0/18.14) = 1,203,000 B.t.u. as the heat removed from the gases or absorbed by the water. Since the

cooling water rises 32°F., the hourly requirement is 1,203,000/32 = 37,600 lb. or 4,520 gal., assuming all the heat thus removed.

Illustration 2.—Pyrites fines are burnt in a Herreschoff burner to form SO_2 for conversion to SO_3 in a sulfuric acid plant. The pyrites used carry 48% S. Analysis of the burner gas shows 9.32% SO_2 and 6.93% O_2. The cinder carries 2.15% S. What per cent of the sulfur fired leaves the burner as SO_3 in the burner gas?

Solution.

Basis.—100 mols of burner gas.

Gas	Mols	Mols O_2
SO_2	9.32	9.32
O_2	6.93	6.93
N_2	83.75	
	100.00	16.25
O_2 to iron in cinder, $\simeq SO_2$ formation, (3/8)9.32 =		3.50
		19.75 = O_2 accounted for
83.75(21/79) =		22.27 = O_2 from air
		2.52 = O_2 disappearance
SO_3 formed = (8/15)2.52 =		1.34 mols

This gives as the per cent of the total sulfur oxidized to SO_3, 100(1.34)/(9.32 + 1.34) = 12.56%, leaving 87.44% as SO_2.

Some of the SO_3 remains in the cinder as adsorbed SO_3 and the remainder goes into the burner gas. The analysis shows the percentage of sulfur in the cinder, and this can be converted to the equivalent percentage of SO_3. First, however, the weight of the SO_3-free cinder is computed. This is done as follows:

Basis.—100 lb. pyrites.

The sulfur fired is 48 lb. and the remainder, 52 lb., is gangue and iron together. The latter is all oxidized to Fe_2O_3 and the gangue is assumed to remain constant in weight. Whether the sulfur is oxidized to SO_2 or SO_3, the equations for combustion of pyrites show that for each 8 atoms of S burnt 3 mols of O_2 combine with the iron. Therefore, the increase in weight of the gangue and the iron as they appear in the cinder is

$$\frac{\text{Pounds S}}{48} \left| \frac{\text{Atoms S}}{32.1} \right| \frac{\text{Mols } O_2}{8} \left| \frac{32}{3} \right. = 18.00 \text{ lb. of } O_2.$$

Hence, the weight of the SO_3-free cinder is $52 + 18 = 70$ lb.

The sulfur in the cinder as adsorbed SO_3 is 2.15% of the weight of the cinder. If x be the number of pounds of sulfur in the cinder, then $(80/32)x$ is the corresponding weight of SO_3 in it and the total weight is $70 + (80/32)x$. From the condition that the percentage of sulfur is 2.15, there is obtained the equation,

$$\frac{100x}{70 + (80/32)x} = 2.15.$$

This gives for x, 1.59 lb. of S. Of the total of 48 lb. of S fired, this sulfur which remains in the cinder as SO_3 is 3.31%. Since 12.56% of the S fired was oxidized to SO_3, $12.56 - 3.31 = 9.25\%$ left the burner as SO_3.

Bisulfites.—The formation of SO_3 has been mentioned as one of the factors which interfere with bisulfite manufacture. This SO_3 formation may take place in the burners as illustrated above and thus be present in the gas entering the absorbing apparatus, or it may take place in the absorbers themselves. Another factor influencing the results is the kind of lime used. The amount of lime necessary to absorb a given amount of SO_2 gas will be different for one containing a high percentage of magnesia than for one consisting of nearly pure CaO, since the equivalent weights of lime and magnesia are not the same.

Illustration 3.—The cooled gas of Illustration 1 is absorbed in a milk of lime, to form bisulfites, in a tower in which the absorbing solution flows countercurrent to the gas. The gas leaves the tower at 76°F., containing 2.8% O_2 and no SO_2. The bisulfite liquor produced is 7.05% total SO_2, of which 1.15% is "free," the rest, 5.90%, being present as bisulfites. The dolomitic lime used is 82% CaO and 16% MgO. Calculate the following:

1. The volume of gas leaving the absorbing tower per minute.
2. The consumption of lime per hour and the water necessary to slake it.
3. The amount of bisulfite liquor produced per hour.

It is, of course, possible to answer items 2 and 3 by actually measuring the quantities involved. On the other hand, the measurement of large quantities of flowing liquids requires the use of equipment often unavailable in connection with such a

process. The ratio of these different quantities to one another is, however, determined by the analytical data. Since these analyses are easily carried out, they are very useful in computing the amounts in the various streams when the size of one of them is known (in this case the sulfur fed to the burners was weighed directly).

SUMMARY OF OTHER DATA AND CALCULATED QUANTITIES

Pounds S (99.4% pure) burnt per hour	680
Per cent of above burning to SO_2	95.9
Cubic feet of air at 60°F. used per minute	743
Analysis of SO_3-free burner gas:	
SO_2	17.4%
O_2	2.7%
Cu. ft. of gas leaving cooler (entering absorber) per min.	753
Temperature of gases leaving cooler	70°F.

1. *Basis.*—1 min.

Cubic feet air at 60°F.	N_2 at 60°F.	Dry waste gas	
743	79	100	536
	100	(100 − 2.8)	520

= 623 cu. ft. dry gas per minute

It must, however, be remembered that this gas is practically saturated with water vapor since the vapor-pressure lowering of water in a saturated lime solution is negligible. The partial pressure of water vapor is, at 76°F., 0.87 in., whence the total volume is

$$623(29.92)/(29.92 - 0.87) = 642 \text{ cu. ft.}$$

2. As a result of the absorption of the sulfurous gases, calcium and magnesium sulfates, bisulfites and free sulfurous acid will be formed. First, it must be shown qualitatively whether any oxidation of SO_2 has taken place in the absorbers, and second, the amount of this oxidation must be calculated; since for every mol of SO_3 (from oxidation of SO_2) going to sulfate, 1 mol of lime or magnesia must be used, whereas only 1 mol of the basic oxides is required for every 2 mols of SO_2 forming bisulfites.

There is available the analysis of the gas entering the tower and of that leaving it. The nitrogen in this gas is practically unchanged; it could disappear in no other way than by solution in the bisulfite liquor. Its solubility in water is so slight as to render this loss negligible, and it is not unlikely that the water employed is originally more or less saturated with it, thus rendering this error even smaller. The nitrogen is, therefore, a suitable basis for comparison of the gas entering and leaving the absorber.

Basis.—100 mols N_2.

Component	Ratio to 100 mols N_2	
	At entrance	At exit
SO_2	17.4/0.799 = 21.78	None
O_2	2.7/0.799 = 3.38	2.8/0.972 = 2.88

Granting no oxidation, the ratio of oxygen to nitrogen should be the same at exit and entrance. However, the analyses show an appreciable decrease.[1] This decrease of 3.38 − 2.88 = 0.50 mol O_2 will oxidize twice that amount of SO_2, or 1.00 mol. Of the total SO_2 entering the tower, therefore, 1.00/21.78, or 4.6%, is oxidized to SO_3. Since only 95.9% of the S burnt enters the absorber as SO_2, the oxidation in the absorber is 4.4% of the sulfur burnt. This makes a total of 8.5 % of all the sulfur burnt which goes to SO_3, since 4.1% had previously been oxidized to SO_3 in the burners. All this enters the absorber, since the air is dry, but had it contained moisture, some or all of the first 4.1% would have been condensed in the coolers as H_2SO_4.

The amount of oxides necessary to absorb the SO_2 and SO_3, respectively, can now be computed.

Basis.—1 hr.

$$\frac{\text{Pounds crude S}}{680} \times \frac{\text{Pounds pure S}}{0.994} \times \frac{\text{Pounds S in liquor as } SO_2}{(1.0 - 0.085)} \times \frac{\text{Mols } SO_2 \text{ in liquor}}{32.1} \times \frac{\text{Mols lime}}{5.90/2} = \frac{\text{Mols CaO + MgO}}{7.05}$$

= 8.06 mols CaO + MgO per hour for the combined SO_2 only

$$\frac{\text{Pounds crude S}}{680} \times \frac{\text{Pounds pure S}}{0.994} \times \frac{\text{S as } SO_3}{0.085} \times \frac{\text{Mols } SO_3}{32.1}$$

= 1.79 mols oxides for SO_3

Basis.—100 lb. lime.

Mols of CaO = 82/56 =	1.463
Mols of MgO = 16/40.3 =	0.397
Mols of total oxides	1.860

[1] Oxidation of SO_2 takes place appreciably in dilute solution.

Basis.—1 hr.

Lime required = (8.06 + 1.79) (100/1.86) = 529 lb. per hour for combined SO_2 and SO_3

The amount of water used can be obtained by deducting from the total weight of the solution the weight of its components other than water. To compute the components in the liquor:

Pounds crude S	Pounds pure S	Pounds S as SO_2	
680	0.994	(1.0 − 0.085)	$\frac{64.1}{32.1}$ = 1,235 lb. SO_2

Pounds crude S	Pounds pure S	Pounds S as SO_3	
680	0.994	0.085	$\frac{80.1}{32.1}$ = 143 lb. SO_3

Total weight of solids = 529 (lime) + 1,235(SO_2) + 143(SO_3) = 1,907 lb.
Total weight liquor = 1,235/0.0705 = ... 17,510 lb.

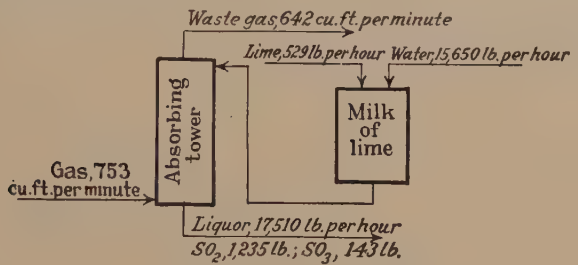

Waste gas, 642 cu.ft. per minute
Lime, 529 lb. per hour
Water, 15,650 lb. per hour
Absorbing tower
Milk of lime
Gas, 753 cu.ft. per minute
Liquor, 17,510 lb. per hour
SO_2, 1,235 lb.; SO_3, 143 lb.

FIG. 6.—Production of bisulfite liquor.

By difference, water in liquor = 17,510 − 1,907 = 15,600 lb. To this must be added the water picked up by the gas, certainly small, but calculated as follows:

The pressure of water vapor at 76°F. is 0.87 in.

Cubic feet gas per hour	Cubic feet H_2O vapor	Cubic feet at S. C.	Mols H_2O	
642 × 60	0.87	492		$\frac{18}{}$ = 51.5 lb. H_2O vaporized per hour
	29.92	536	359	

The total water used is, therefore, 15,650 lb. per hour. See Fig. 6.

3. The weight of bisulfite liquor produced per hour was calculated above to be 17,510 lb.

Sulfuric Acid.—Owing to the corrosive character of sulfuric acid, its measurement when in movement is difficult unless special equipment is already installed in the plant. It is measured directly only when necessary or where the measurement is a normal plant operation, such as the determination of production.

The H_2SO_4 made in the Glover tower is about 12 to 15% of the entire acid produced by the plant, and the fraction may even run as high as 20%. Besides the production of H_2SO_4, one of the important functions of the Glover tower is to concentrate the chamber acid by the evaporation of water from it. It is, therefore, important to be able to compute how much of the total H_2SO_4 is actually produced in the Glover tower and how much water is actually evaporated there in a given plant.

The performance of the Glover tower is so interwoven with the operation of the other units of a chamber plant that its calculation generally involves the calculation of the other factors at the same time. The problem below illustrates the method by which this information can be found.

Illustration 4.

TABULATED DATA

Burner gas:		Nitrous vitriol:	
SO_2	7.90%	N_2O_3 content as per cent $NaNO_3$	2.60
O_2	12.75%	Mixed nitrous vitriol and chamber acid fed to Glover tower:	
N_2	79.35%		
Gas leaving Glover tower:		N_2O_3 content as per cent $NaNO_3$	1.64
SO_2	6.90%	Air temperature:	
O_2	12.40%	Dry bulb	57°F.
N_2	80.70%	Wet bulb	51°F.
Glover tower acid:		Barometer	29.45 in.
Tons per day	20.25		
Gravity (Bé.)	60.5°		
Chamber acid:			
Tons per day	5.50		
Gravity (Bé.)	52.6°		
Sulfur:			
Tons per day	6.70		
Purity	99.4%		

Calculate from these data:

1. The sulfur efficiency.
2. The per cent of the total acid made in the Glover tower.
3. The per cent of the chamber acid returned to the Glover tower for concentration.

4. The water evaporated in the Glover tower.

5. The water fed to the chambers, as steam or otherwise.

6. The ratio of the acid circulated through the Gay-Lussac tower to the acid produced by the Glover tower.

7. The $NaNO_3$ content of the nitrous vitriol, expressed as per cent of the sulfur burnt.

Solution.—1. As the compositions of the Glover and chamber acids are different, these cannot be added together directly to get the plant output, before first being converted to a common basis. Similarly, the sulfur input must also be upon the same basis before the efficiency can be figured. Accordingly, the amounts of these acids and the sulfur burnt will be converted to the equivalent of 100% H_2SO_4, and all other amounts throughout the solution of this problem will, in general, be expressed as or converted to 100% H_2SO_4, unless otherwise stated.

The Glover acid (60.5°Bé. = 78.55%H_2SO_4) will be 20.25(0.7855) = 15.90 tons and the chamber acid (52.6°Bé. = 66.03% H_2SO_4), 5.50(0.6603) = 3.63 tons, giving for the total production 15.90 + 3.63 = 19.53 tons of 100% H_2SO_4 per day. If all the sulfur used in the burners were completely converted to H_2SO_4, the production would be 6.70(0.994)(98/32) = 20.40 tons. Hence, the efficiency of the process is 100(19.53/20.40) = 95.7%. See Fig. 7.

2. *Basis.*—100 mols of burner gas as analyzed.

Gas	Mols	Mols O_2
SO_2	7.90	7.90
O_2	12.75	12.75
N_2	79.35	
Total	100.00	20.65 O_2 accounted for
79.35(21/79) =		21.09 O_2 from air
		0.44 O_2 to SO_3

SO_3 = (2/3)0.44 = 0.30 mol
Total S burnt = 7.90 + 0.30 = 8.20 atoms
S converted to H_2SO_4 = 8.20(0.957) = 7.85 atoms

The data which will show the amount of SO_2 converted to H_2SO_4 in the Glover tower will be the compositions of the gases entering and leaving it. The analyses of the two gases show that they are entirely different with regard to each constituent;

therefore, they are not on the same basis. Actually, the gas leaving contains less SO_2 and O_2 but the same amount of N^2, since the latter element passes through unchanged, and it can, consequently, be made the basis of comparison. Using the same basis as previously, *i.e.*, 100 mols of burner gas or 79.35 mols of N_2, the percentage composition of the gas leaving the Glover tower can be changed to the molal composition on this basis by multiplying by the ratio of the nitrogen contents of the two gases, *viz.*, by 79.35/80.70. Using this factor, the analysis of the gas leaving the Glover tower can be arranged as follows:

GAS LEAVING GLOVER TOWER

Basis.—100 mols burner gas as analyzed.

Gas	Per cent	Factor	Mols
SO_2	6.90	79.35/80.70	6.78
O_2	12.40	79.35/80.70	12.19
N_2	80.70	79.35/80.70	79.35
Total	100.00	.....	98.32

Comparison of these results with the tabulation of the burner-gas data shows that the SO_2 decrease is 7.90 − 6.78 = 1.12 mols

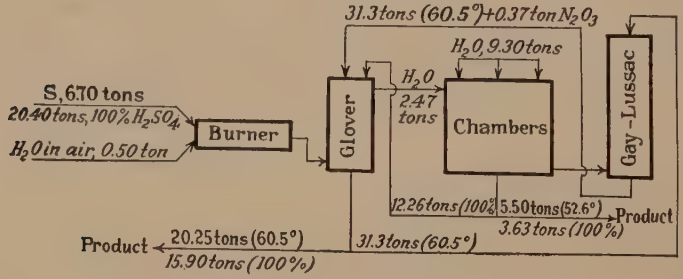


FIG. 7.—Sulfuric acid problem. *Basis.*—24 hr.

and the oxygen decrease, 12.75 − 12.19 = 0.56 mol. Of the total sulfur made into H_2SO_4 (7.85 atoms) the conversion in the Glover tower amounts to (1.12/7.85)100 = 14.3%. However, any SO_3 in the burner gas condenses as H_2SO_4 in the Glover tower. The amount of such SO_3 has been shown to be 0.30 mol. The total SO_3 converted to acid in the Glover tower is, therefore, 100(1.12 + 0.30)/7.85 = 18.1% of the entire plant production. This value will be used in later calculations.

3. The total production of the plant was calculated to be 19.53 tons of 100% H_2SO_4, giving 19.53(0.181) = 3.64 tons as the acid formed in the Glover tower. From the bottom of this tower 15.90 tons are drawn off as product, and the difference, 15.90 − 3.64 = 12.26, represents the chamber acid which is concentrated in the Glover tower. This is $\frac{12.26}{12.26 + 3.63} \times 100 =$ 77.1% of the total acid formed in the chambers which is returned to the Glover tower for concentration.

4. The water evaporated in the Glover tower is determined by a water balance. The input consists of the water fed to the top of the tower in the form of mixed acid, made by mixing chamber acid with the nitrous vitriol from the Gay-Lussac tower, and of the water vapor in the air used for combustion. The water output of the tower includes the water in the acid issuing from the bottom and that evaporated, which leaves the top of the tower and passes to the first chamber along with the other gases.

A simplification is made by assuming that no water is gained or lost by the H_2SO_4 circulated through the Gay-Lussac tower. A small quantity of acid mist and water is carried over into the Gay-Lussac tower by the gases leaving the last chamber, but this is negligible compared to the quantity of acid passing through the tower. The water input to the top of the Glover tower due to the nitrous vitriol is then equal to the water output in the acid from the bottom which is sent to the Gay-Lussac tower. Hence, the water input may be treated as the water brought in by the chamber acid plus the water vapor in the burner gas (originally from the air), and the water output as that in Glover acid drawn off as product plus the water evaporated.

The dry-bulb temperature of the air is given as 57°F. and the wet-bulb temperature as 51°F. The humidity of the air under these conditions is found from humidity tables to be 66%. At 57°F. the vapor pressure of water is 0.47 in., so that its partial pressure in the air used is 0.31 in. The barometer is 29.45 in., whence the pressure of the dry air is 29.45 − 0.31 = 29.14 in.

The water vapor entering the burners and hence the Glover tower due to the humidity of the air, expressed as tons per day, is as follows:

Tons crude S	Ton atoms S	Ton mols N_2	Ton mols air	Ton mols H_2O		
6.70	0.994	79.35	100	0.31	18	
	32.1	8.11	79	29.14		= 0.50 ton.

The chamber acid contains 66.03% H_2SO_4, the rest being water, so that the amount of the latter entering the Glover tower from this source is 12.26(33.97/66.03) = 6.31 tons. The total input of water, exclusive of that contained in the nitrous vitriol, is the sum of these two quantities, 6.31 + 0.50 = 6.81 tons.

The water output in the form of Glover acid, exclusive of that returned to the Gay-Lussac tower, is

$$15.90 \times 21.45/78.55 = 4.34 \text{ tons.}$$

Consequently, the rest of the output, or 6.81 − 4.34 = 2.47 tons, is evaporated by the hot gases entering the Glover tower.

5. With the exception of 0.50 ton of water entering with the air, the rest of the water in the product, both that combined with SO_3 to give H_2SO_4 and that used to give dilute acid, is added to the chambers.

The tons of water in the Glover and chamber acids above that necessary to make 100% H_2SO_4 are 15.90(21.45/78.55) = 4.34 tons and 3.63(33.97/66.03) = 1.87 tons, respectively. That combined with SO_3 to give H_2SO_4 amounts to 19.53(18/98) = 3.59 tons. The total, less 0.50 ton from the air, is that fed to the chambers: 4.34 + 1.87 + 3.59 − 0.50 = 9.30 tons.

6. The analysis of the nitrous vitriol is given as equivalent to 2.60% $NaNO_3$ and that of the acid formed by mixing it with chamber acid is given as equivalent to 1.64% $NaNO_3$. Consequently, the weight of the nitrous vitriol will be to the weight of the mixed acid inversely as the ratio of the equivalent $NaNO_3$ contents, or as 1.64:2.60. The weight of the chamber acid in the mixed acid is 12.26/0.6603 = 18.55 tons, so that, calling the weight of the nitrous vitriol x, the above becomes

$$\frac{x}{18.55 + x} = \frac{1.64}{2.60},$$

giving 31.7 tons as the weight of the nitrous vitriol.

Part of this consists of the N_2O_3 content, *i.e.*, (31.7)(0.0260)(38/85) = 0.37 ton, leaving 31.7 − 0.37 = 31.3 tons as the weight of 60.5° Bé. Glover acid circulated through the Gay-Lussac tower. This is 31.3/20.25 = 1.55 times the quantity of Glover acid drawn off as product.

7. The equivalent $NaNO_3$ content of the nitrous vitriol is 31.7(0.0260) = 0.825 ton, or, expressed as a percentage of the sulfur burnt, (0.825/6.70)100 = 12.3%.

PROBLEMS

1. Sulfur is to be burnt at the rate of 400 lb. per hour to produce SO_2 for production of bisulfite liquor used in the manufacture of wood pulp. It is proposed to use 10% excess air. It is estimated that the gases will enter the flue leading to the coolers at 650°C. Furthermore, it is desired to have the linear velocity of the gases at this point 5 ft. per second.

(*a*) What should be the diameter of the flue? *Ans.* 2.38 ft.

(*b*) The gases leave the absorbing tower at 60°F. What must be the volumetric capacity of the suction blower in cubic feet per minute? *Ans.* 335.

2. A contact sulfuric-acid plant using sulfur as raw material uses a number of contact chambers with SO_3 absorbers after the first and last chambers. The gas leaving the absorber after the first chamber has 6.0% SO_2 and 7.0% O_2. What per cent of the total sulfur burnt is oxidized to SO_3 previous to this point? *Ans.* 52.9%.

3. In a plant producing H_2SO_4 by the contact process, sulfur is burnt to SO_2 in a suitable burner, and the SO_2 gases pass through a preliminary contact chamber in which partial oxidation to SO_3 occurs. This SO_3 is absorbed and the gases then pass to a final contact chamber and absorber. The gases leaving the first absorber are 3.35% SO_2 and 8.27% O_2.

(*a*) Of the total sulfur burnt, what per cent is oxidized to SO_3 in the first contact chamber?

(*b*) What per cent of excess air was used over that theoretically required for complete oxidation? *Ans.* 39.2%.

(*c*) Assuming complete oxidation in the final chamber, followed by quantitative absorption of the SO_3, what is the per cent of oxygen in the gas discharged from the system? *Ans.* 6.95%.

4. A contact sulfuric acid plant pays 14.4 cts. per unit (*i.e.*, price per ton divided by per cent of total sulfur), f.o.b. mine, and $1 freight per ton of ore of the following analysis:

	Per Cent
S	47.40
Cu	1.70
As	0.39
Fe	46.20
Pb	0.47
Zn	0.12
Gangue	3.72

The cinder is found to contain 5.2% S, and the arsenic, lead and zinc are largely volatilized. The gangue remains unaffected, except that lime and magnesia go to sulfates. The plant also recovers 80% of the copper by leaching the cinder, at a net profit of 9 cts. per pound of copper recovered. Of the total SO_2 gases going to the contact chamber, 4% pass through unoxidized. What is the net raw material cost (allowing for copper recovered) per ton of 100% H_2SO_4 produced? *Ans.* $3.48.

5. A plant is using pyrites *A*, paying 16.4 cts. per unit, f.o.b. mine, the freight rate being $1 per ton of ore.

	Pyrites *A*, per cent	Pyrites *B*, per cent
S	49.70	49.40
Cu	3.12	0.46
As	0.72	0.39
Fe	44.00	46.20
Pb	0.86	0.47
Zn	0.38	0.12

In the cinder from burning *A* as well as possible, there is 4.1% S, but it is estimated that the cinder from *B* will have only 3.2%. This plant leaches the cinder from *A*, recovering 90% of the copper at a cost of 4 cts. per pound of copper recovered, its value (less selling costs, etc.) being 12 cts., leaving a net profit of 8 cts. per pound of copper. Per unit of sulfur, what can the plant afford to pay for *B*, f.o.b. mine, the freight rate being 50 cts. per ton? (See problem 4.) *Ans.* 9.85 cts.

6. Pyrites fines are burnt in a Herreshoff burner to form SO_2 for conversion to SO_3 in a chamber sulfuric acid plant. The pyrites used carry 46.5% S. The cinder produced carries 2.03% S. The burner gases contain 9.58% SO_2 and 7.51% O_2. The gases are sampled after each chamber, the nitrogen oxides removed from the sample and the residual sample analyzed over mercury. The following results are the averages of a number of analyses:

	After first chamber, per cent	After second chamber, per cent	After third chamber, per cent
SO_2	4.87	1.28	Trace
O_2	5.37	3.74	3.16
N_2	89.76	94.98	96.84

(*a*) What per cent of the sulfur fired leaves the burner as SO_2 in the burner gas? *Ans.* 92.8%.

(*b*) What per cent of the sulfur fired is converted into and condensed as H_2SO_4 in each chamber, assuming no SO_3 passes from one chamber to the next? *Ans.* 49.2%, 32.8%, 10.8%.

7. A plant burns sulfur of 99.6% purity at the rate of 720 lb. per hour. The average air temperature is 75°F., and the pressure of the water vapor in it is 18 mm. The barometer is normal. The gases leave the burner at 700°C., and when analyzed over mercury contain 15.5% SO_2, 4.5% O_2 and the rest N_2. The gases pass through a cooler, and leave the cooler at 65°F. They then are passed through a coke tower, to remove from them any sulfuric acid mist which may be formed in the cooler. The gases pass from the coke tower to an absorbing tower, where they are brought into contact with milk of lime to form bisulfites. The gases leave the tower at 70°F., and contain 4.7% O_2 and no SO_2. The bisulfite liquor produced contains

6.95% total SO_2, of which 1.25% is "free," the rest, 5.70%, being present as bisulfites. The lime used is 80% CaO and 16% MgO. Calculate the following:

(*a*) Per cent of total sulfur burnt to SO_3 in the burner. *Ans.* 5.2%.

(*b*) The air consumption in cubic feet per minute. *Ans.* 927.

(*c*) The heat dissipated from the burner in B.t.u. per hour. *Ans.* 880,000.

(*d*) The volume of gas leaving the absorbing tower per minute. *Ans.* 754 cu. ft.

(*e*) The lime consumption, pounds per hour. *Ans.* 536.

(*f*) The pounds of bisulfite liquor produced per hour. *Ans.* 17,750.

8. In the making of wood pulp by the bisulfite process, crude sulfur containing 2% of non-volatile impurity is burnt, the gases are cooled and then mixed with "recovered" gas from the digesters in which the wood pulp is cooked with the bisulfite liquor. The mixed gases are absorbed by milk of lime, thus giving the bisulfite liquor. The following data are the average results of a number of analyses.

	Gas leaving cooler, per cent	Recovered gas, per cent	Mixed gases to absorber, per cent
SO_2	19.20	50.00	21.45
O_2	1.70	6.53	2.05
N_2	79.10	43.47	76.50

(*a*) Calculate the per cent excess air fed to the burner. *Ans.* 9.03%. Calculate per pound of crude sulfur fired:

(*b*) Cubic feet of air to burner (dry, S.C.). *Ans.* 45.0.

(*c*) Cubic feet of recovered gas (dry, S.C.). *Ans.* 3.6.

9. A gas works is removing H_2S from impure gas from the ammonia scrubbers by the use of an iron ore containing on the average 34% Fe_2O_3 and no S. Air is admitted by a separate duct to the purifiers so that the revivification is continuous. When the purifying agent is rejected, the analysis is 16% Fe_2O_3 and 46% S. A ton of ore is required for each 1,200,000 cu. ft. of purified gas measured at standard conditions.

Calculate:

(*a*) The volume of gas removed in the purifiers per 1,000 cu. ft. of purified gas. *Ans.* 18.3 cu. ft.

(*b*) The volume of air theoretically required per 1,000 cu. ft. of impure gas entering the purifiers. *Ans.* 44.2 cu. ft.

(*c*) The number of times the iron may be considered to have been reused, assuming an average of 75% conversion each time. *Ans.* 5.4.

(*d*) The increase in the per cent of nitrogen in the final product due to the admitting of the theoretical amount of air. *Ans.* About 3.4%.

TROJAN POWDER COMPANY

CHAPTER V

LIME AND CEMENT

In lime burning the fuel consumption is often expressed as the "fuel ratio," *i.e.*, the pounds of lime produced per pound of fuel used. The fuel ratio can easily be estimated from the analysis of the kiln gas, provided the compositions of fuel and limestone are known.

Illustration 1.—Consider the burning of pure calcium carbonate with hydrogen-free coke containing 83% carbon producing a gas of the composition 26.5% CO_2, 5.0% O_2 and 68.5% N_2. It is required to compute the ratio of lime produced to coke burnt, the per cent excess air used in combustion and the amount of stack gas per ton of lime.

Solution.—This problem differs from one in simple combustion in that the gas contains not only the products of combustion of the fuel but also a reaction product from the charge, *i.e.*, the CO_2 from the limestone. In calculation, this must in some way be separated from the rest of the CO_2, which is a product of combustion. The nitrogen present in the gas comes wholly from the air used for combustion of the fuel and may be employed as the basis of an oxygen balance in the manner illustrated under combustion calculations. The free oxygen in the kiln gas is due to excess air and, allowing for this, the nitrogen will give the oxygen actually consumed in the combustion of the fuel. The following computation should be self-explanatory.

Basis.—100 mols of dry kiln gas.

Component	Mols	Mols O_2	Atoms C
CO_2	26.5	26.5	26.5
O_2	5.0	5.0	
N_2	68.5		
Total	100.0	31.5	
O_2 from air, 68.5(21/79) =		18.2	
$\therefore$ O_2 from stone = CO_2 from stone =		13.3	13.3
$\therefore$ C from fuel = O_2 for combustion =		13.2	13.2

$\therefore$ weight CaO produced = 13.3(56.1) = 745 lb.
$\therefore$ weight coke burnt = 13.2(12)/0.83 = 191 lb.
$\therefore$ fuel ratio = lb. CaO/lb. coke = 745/191 = 3.9.
Per cent excess air = 100(5.0/13.2) = 37.9%.
Mols kiln gas per ton CaO, 2,000(100/745) = 268.

Illustration 2.—In practice, however, pure $CaCO_3$ is not used as the source of the lime nor coke as the fuel. For example, a limestone containing, on the dry basis, 42.5% CO_2 and no other volatile matter is burnt with coal containing 79.8% C, 4.7% H, 0.5% S, 1.8% N, 4.6% O and 8.6% ash. The analysis of the stack gas is 24.4% CO_2, 4.1% O_2 and 71.5% N_2. Compute as in the previous case the fuel ratio, the excess air and the stack gas per ton of lime.

Solution.—Since the coal contains hydrogen, all the oxygen consumed in burning the fuel will not be present in the dry gas, and the previous method must be modified. Preliminary calculations on the coal analysis are necessary.

Basis.—100 lb. coal.

Constituent	Pounds	Mols or atoms	O_2 required
C	79.8	6.75	6.75
H_2	4.7	2.33	
O_2	4.6	0.14	
Net H_2	....	2.05	1.03
Total	....	....	7.78

This table shows that, whereas 100 lb. of coal contain 6.75 atoms of C, to burn this coal 7.78 mols of atmospheric oxygen are required, of which 1.03 mols will not appear in the kiln-gas analysis, since it represents oxygen combining with net hydrogen to form water.

Now consider the gas. Obviously, the oxygen present as such in the gas is due only to excess air.

Basis.—100 mols dry gas.

O_2 from air, 71.5(21/79)	19.0 mols
O_2 excess	4.1 mols
O_2 required for combustion	14.9 mols
Total C present	24.4 atoms
C from coal, 14.9(6.75/7.78)	12.9 atoms
C from limestone	11.5 atoms
Pounds lime, 11.5(44)(100 − 42.5)/42.5[1] =	685
Pounds coal, 12.9(100/6.75) =	191
Pounds lime per pound of coal, 685/191 =	3.59
Excess air, 100(4.1/14.9) =	27.5%
Mols H_2O from combustion, 14.9(2.33/7.78) =	4.46
Total stack gas, 100 + 4.46 =	104.46
Mols gas per ton of lime, 2,000(104.46/685) =	305

It will be noted that this method involves earmarking and setting aside the excess oxygen, leaving 14.9 mols as the oxygen necessary for theoretical combustion. Since the analysis of the fuel gives the ratio of carbon in the fuel to oxygen required for theoretical combustion, it is now possible to earmark the carbon from the fuel and get the carbon from the stone by difference.

The above examples serve to indicate the method of computation. The ones which follow show how the method is applied to gas-fired kilns and kilns provided with gas-recirculation equipment.

Illustration 3.—A gas producer supplies the fuel for several lime kilns. Although the composition of the gas varies, the average of a number of analyses gives 9.5% CO_2, 20.1% CO, 11.3% H_2, 2.8% CH_4 and 56.3% N_2. Samples of the gas discharged by the kiln give 27.75% CO_2, 2.25% O_2 and 70.0% N_2. Find per pound of carbon burnt the number of pounds of lime produced from a limestone of the composition 1.54% insoluble, 1.44% R_2O_3 (small iron), 50.07% CaO and 3.54% MgO.

Solution.—Examination of the kiln-gas analysis shows that its carbon comes from the producer gas and the limestone, its

[1] The figure 44 is the molecular weight of CO_2.

oxygen from three sources, fuel, limestone and air, and its nitrogen from both air and fuel. Furthermore, the hydrogen in the fuel does not appear in the dry kiln gas. While the selection of a basis for calculation is somewhat arbitrary, there being no single factor connecting one stream with the others, nevertheless, as in the preceding cases, it will be found convenient to choose the kiln gas as the basis of computation.

Basis.—100 mols of dry kiln gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	27.75	27.75	27.75
O_2	2.25	.....	2.25
N_2	70.0		
Total	100.0	27.75	30.00

Now, since the quantities of the other three streams yielding this kiln gas are not determinable directly, let

x = the mols of producer gas.
y = the mols of air.
z = the mols of CO_2 from the limestone.

Next the data from the analysis of the fuel are tabulated:

Basis.—100 mols of dry producer gas.

Gas	Mols	Atoms C	Mols H_2	Mols O_2
CO_2	9.5	9.5	....	9.5
CO	20.1	20.1	....	10.05
H_2	11.3	....	11.3	
CH_4	2.8	2.8	5.6	
N_2	56.3			
Total	100.0	32.4	16.9	19.55

Three simultaneous equations can be written expressing carbon, oxygen and nitrogen balances:

C balance, $0.324x + z = 27.75$
O_2 balance, $(0.1955 - 0.169/2)x + 0.21y + z = 30.00$
N_2 balance, $0.563x + 0.79y = 70.00$

The term, $(0.1955 - 0.169/2)x$, in the O_2 balance is the oxygen in the producer gas going into the dry kiln gas. It is obtained

by subtracting from the total oxygen in the fuel the oxygen equivalent of the hydrogen in it, because $(0.169/2)x$ mols of oxygen will not show up in the dry kiln gas. These equations when solved give:

x = 45.1 mols of producer gas.
y = 56.5 mols of air.
z = 13.13 mols of CO_2 from the limestone.

Another solution to the problem, not algebraic, follows:

Basis.—100 mols producer gas. The oxygen required for theoretical combustion is 32.4 + 16.9/2 − 19.55 = 21.3 mols, the corresponding amount of nitrogen being 21.3(79/21) = 80.2 mols. Adding this to the nitrogen already present in the fuel gives 136.5 mols as the total nitrogen produced by theoretical combustion. Hence, the ratio of carbon from the fuel to total theoretical nitrogen is 32.4/136.5.

Basis.—100 mols dry kiln gas. Turning attention again to the kiln gas, it is seen that this contains 2.25 mols of O_2, the presence of which is due to excess air. The corresponding nitrogen is 2.25(79/21) = 8.47 mols. The remaining nitrogen, 70.00 − 8.47 = 61.53 mols, may be designated as the necessary nitrogen coming from the theoretical combustion of the fuel. Since the ratio of carbon in the fuel to the necessary nitrogen has been calculated to be 32.4/136.5, the actual amount of CO_2 from the fuel present in 100 mols of kiln gas must be (32.4/136.5)61.53 = 14.62 mols. The remainder, 27.75 − 14.62 = 13.13 mols, comes from the limestone. To calculate the amount of producer gas used, it will be noted that it must be sufficient to give 14.62 mols CO_2. Since 100 mols of producer gas will yield 32.4 mols of CO_2, (100/32.4)14.62 = 45.1 mols of producer gas will be necessary.

This solution involves earmarking and setting aside the nitrogen equivalent to excess air, the remaining nitrogen being that corresponding to theoretical combustion. Since the analysis of the fuel gives the ratio of the carbon in the fuel to the nitrogen for theoretical combustion, it is now possible to earmark the carbon from the fuel and get that from the stone by difference. This illustrates the fact that earmarking frequently makes it possible to simplify computation by using arithmetic methods rather than algebraic. Algebraic methods, however, though sometimes more cumbersome, are more generally applicable.

The above results show that 45.1 mols of producer gas are required for 13.13 mols of CO_2 produced from the stone. This gas is equivalent to 45.1(32.4/100)(12) = 175.5 lb. of carbon consumed in the producer. If the per cent of carbon in the coal is known, this figure can be converted into the corresponding weight of the coal. Then, in order to calculate the final result, namely, the pounds of lime produced per pound of carbon consumed, the only remaining quantity to be determined is the pounds of lime produced, which will be obtained through the analysis of the limestone.

Basis.—100 lb. limestone.

	Pounds Non-volatile
Insoluble	1.54
R_2O_3	1.44
CaO	50.07
MgO	3.54
Total non-volatile	56.59

CO_2 by difference = 43.41 lb. = 0.985 mol.

The figure, 43.41, obtained by difference from 100 of the sum of the other constituents may be checked against the CO_2 corresponding to the CaO and MgO present. Theoretically, the CO_2 should be 50.07(44/56.1) + 3.54(44/40.3) = 43.15%. The useful datum obtained from this analysis is the ratio, pounds of lime (non-volatile material):mols of CO_2, which is 56.59/0.985.

Returning to the former basis of 100 mols of kiln gas, 175.5 lb. of carbon burnt in the producers are equivalent to 13.13 mols of CO_2 from the limestone which produces (56.59/0.985) 13.13 = 755 lb. of lime. The ratio, pounds of lime per pound of carbon, is 755/175.5 = 4.3.

Illustration 4.—An externally fired shaft lime kiln uses a coal of 14,160 B.t.u. per pound as fired, which contains 78.31% C, 5.26% H, 1.55% N, 0.90% S, 6.37% ash and 7.61% O. The kiln burns a limestone of high purity, producing on the average 2,000 lb. per hour of burnt lime. The average stack-gas analysis is 19.1% CO_2, 6.8% O_2 and 74.1% N_2. These gases leave the kiln at 300°C., and the lime is discharged at 250°C., air temperature being 20°C.

The heat of formation of $CaCO_3$ from CaO and CO_2 at 20°C. is 42,500 cal. per gram mol. The specific heat of CaO may be

taken as 0.18, while that of $CaCO_3$ is $0.202 + 0.0001t$, where t is in degrees Centigrade.

Compute the following:

1. Fuel ratio, *i.e.*, the pounds of lime per pound of coal.
2. Excess air used for combustion.
3. Heat distribution in the kiln.

Solution.—In order to get the coal and gas analyses into more useful shape, they will be recalculated as follows:

Basis.—100 lb. of coal.

	Pounds	Mols or atoms	O_2 required	H_2O
C	78.31	6.52	6.52	
H_2	5.26	2.61	....	2.61
S	0.90	0.03		
O_2	7.61	0.24		
Net H_2	....	2.22	1.11	
			7.63	

Sulfur will be converted to SO_3 in this kiln, being absorbed by the lime as $CaSO_4$. Deducting the amount of oxygen

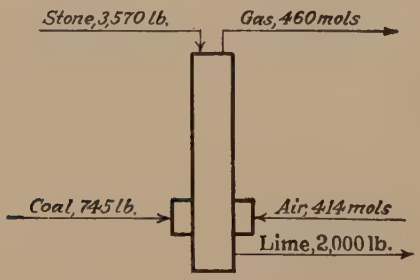


FIG. 8.—Lime kiln. *Basis.*—1 hr.

required for this from the oxygen present gives for the net oxygen, $0.24 - (3/2)(0.03) = 0.195$ and for the net hydrogen, $2.61 - 2(0.195) = 2.22$ mols.

Basis.—100 mols of stack gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	19.1	19.1	19.1
O_2	6.8	....	6.8
N_2	74.1		
Total	100.0	19.1	25.9

From this table the following can also be computed (See Fig. 8):

O_2 in entering air, 74.1(21/79)	19.7
O_2 in excess	6.8
O_2 required for complete combustion	12.9
Total C present	19.1
C from coal, 12.9(6.52/7.63) =	11.0
C from stone	8.1
Lime produced, 8.1(56.1) =	454 lb.[1]
Coal used, 11.0(100/6.52)	169 lb.
Pounds lime per pound coal, 454/169 =	2.68
Per cent of excess air, 100(6.8/12.9) =	52.7%
Mols H_2O from combustion, 2.61(12.9/7.63) =	4.4 mols
Mols gas passing through shaft per pound of lime produced, 104.4/454 =	0.23 mol

On an hourly basis:

Pounds of lime produced	2,000 lb.
Pounds of coal used, 2,000(169/454) =	745 lb.

In computing the heat distribution, since the temperatures are all given in Centigrade, it will be convenient to perform the calculations in C.h.u. rather than B.t.u. The heat of combustion of the coal is 14,160/1.8 = 7,870 C.h.u. per pound, which is the higher heating value. Since the water formed on combustion will be vaporized, this should be lowered by the amount necessary to do this. Using 10,500 C.h.u. per mol of water as the heat of vaporization, this will give 7,870 − 10,500 (2.61/100) = 7,595 C.h.u. Thus the heat input will be the number of pounds of coal times the lower heating value, 745 (7,595) = 5,650,000 C.h.u.

[1] Exclusive of the SO_3 absorbed, 0.03(12.9/7.63)80 = 4 lb.

The heat output is made up of the sensible heat in the stack gas, the sensible heat in the hot lime, the heat of decomposition and the radiation loss.

The sensible heat in 100 mols of dry gas plus 4.4 mols of water vapor at 300°C. above 20°C. is found by using Fig. 1 (p. 5).

Basis.—100 mols of dry stack gas.

Gas	Mols	Heat content, C.h.u.		Difference, C.h.u.	Sensible heat, total C.h.u.
		At 300°C.	At 20°C.		
CO_2	19.1	2,920	180	2,740	52,400
N_2, O_2	80.9	2,070	140	1,930	156,000
H_2O	4.4	2,530	170	2,360	10,400
Total	104.4	.....	...	.....	218,800

This and the other items of heat output will be calculated per hour.

Basis.—1 hr.

	C.h.u.	Per cent
Stack-gas loss per hour:		
(218,800/454)2,000 =	964,000	
(964,000/5,650,000)100 =	.....	17.0
Heat in lime:		
2,000(0.18)(250 − 20) =	82,800	
(82,800/5,650,000)100 =	.....	1.5
Heat of decomposition:		
(2,000/56.1)42,500 =	1,515,000	
(1,515,000/5,650,000)100 =	.....	26.8
Total heat accounted for	2,562,000	45.3
Heat loss by radiation, by difference	3,088,000	54.7
Total heat output = heat input	5,650,000	100.0

This kiln has an excessive fuel consumption, due to an inordinately large radiation loss. It should be examined to determine the cause of this loss and the defect remedied if practicable.

Illustration 5.—It is proposed to provide the kiln of the preceding problem with Eldred-Doherty recirculation to reduce fuel consumption and to protect the lime from overburning. To

accomplish this, the kiln will be operated with only 20% excess air and the recirculation and furnace operation so adjusted that the furnace gases enter the kiln at 1100°C. Furthermore, these furnace gases entering the kiln are to contain enough CO and hydrogen so that the heat of their combustion will furnish the total heat of decomposition of the stone at burning temperature. The lime is to be burnt at 900°C. All preheating of the stone will be done at the expense of the sensible heat of the kiln gases. No attempt will be made to increase kiln capacity. This being the case, the same temperatures may safely be assumed for stack gases and burnt lime as under present operating conditions, *i.e.*, 300 and 250°C. respectively. Furthermore, wall losses by radiation and conduction will remain unchanged. It is estimated that, of these total wall losses, 5% occur in the cooling zone, 10% in the lime-burning zone, 15% from the external furnace and 70% from the charge-preheating zone in the upper part of the shaft and stack connections.

These assumptions appear to imply a sharp demarcation between the zones of preheating and burning the stone, whereas, of course, these zones overlap decidedly. Such overlap, however, does not affect the heat distribution on the assumptions as stated. Actually some residual CO and hydrogen may burn in the preheating zone, but in so far as this is the case the gases cool correspondingly in decomposing the stone. Effects of this sort must counterbalance completely and, therefore, need not be considered in computation.

The molal ratio of $CO:H_2$ in the furnace gases may be taken as 4:1. Even if this ratio be greatly in error, it makes but little difference in the results, because the heats of combustion of the two are so nearly equal.

To design the recirculating equipment, it is necessary to know the amount of gas to be handled and, to justify the installation, the saving in fuel. Therefore, the following should be computed:

1. The percentage saving in fuel which may be anticipated from the modified equipment.
2. The volume of stack gases which must be recirculated per hour.
3. Percentage of the total air supply which enters the furnace and percentage entering the bottom of the kiln as secondary air.
4. Analysis of the furnace gases entering the kiln.

Solution.—Examination of the problem shows that the data given are the coal analysis, the amount of lime produced, the per cent excess air, certain temperature requirements, certain physical characteristics of the materials, such as specific heats and heats of reaction, and the radiation loss. The problem then involves several unknown quantities. One of these is the fuel consumption which will be called x. Now the total air used is a function of x and so also is the quantity of stack gas. An overall heat balance will give the value for x. The fact that some gas is recirculated does not influence the gas analysis, for, as a certain amount of the gas enters the furnace at 300°C., a like amount is discharged from the top of the kiln.

Therefore, consider a section around the whole kiln. The streams of materials entering this system are the coal, the air and the stone, while the streams leaving are the lime and the waste gas.

Basis.—1 hr. The heat input to the system is $7{,}595x$ C.h.u. The heat output consists of the stack loss, the sensible heat in the lime, the heat of decomposition and the radiation loss. The last three items remain the same as in the previous case, but the stack loss is different. Upon formation of 2,000 lb. of lime, there will be evolved $2{,}000/56.1 = 35.7$ mols of CO_2. The tabulation of the coal analysis given in the solution of Illustration 4 shows the amounts of CO_2 and H_2O formed and of oxygen required for combustion. The combustion products may, therefore, be tabulated.

Source	CO_2	O_2	N_2	H_2O
Stone	35.7			
Coal	$0.0652x$	.....	.....	$0.0261x$
Theoretical air	.....	.....	$(0.0763x)(79/21)$	
Excess air	.....	$(0.0763x)0.2$	$(0.0763x)(0.2)(79/21)$	
Total	$35.7 + 0.0652x$	$0.0153x$	$0.3442x$	$0.0261x$

The heat contents of these gases between 20 and 300°C. have already been calculated (p. 88); therefore the stack loss is

$$(35.7 + 0.0652x)(2{,}740) + (0.3442 + 0.0153)(x)(1{,}093) + (0.0261x)(2{,}360) = 97{,}900 + 934x.$$

The heat balance may now be written, using the values for the

heat of decomposition, heating of lime and radiation loss as before (p. 88):

$$7{,}595x = (97{,}900 + 934x) + 82{,}800 + 1{,}515{,}000 + 3{,}088{,}000,$$

giving $x = 718$ lb. of coal.

With the present installation the fuel consumption per hour is 745 lb. This means a saving of 27 lb. or of $(27/745)(100) = 3.6\%$. Consequently, if the installation be justified, it must be on other grounds than the saving in fuel.

Since 718 lb. of fuel will be required, the amount of waste stack gas and its composition can now be found. See also Fig. 9.

	Function	Amount $x = 718$	Fraction	Per cent
CO_2	$35.7 + 0.0652x$	82.6	82.6/340.6	24.2
O_2	$0.0153x$	11.0	11.0/340.6	3.2
N_2	$0.3442x$	247.0	247.0/340.6	72.6
		340.6	.....	100.0
H_2O	$0.0261x$	18.7		
Total stack gas	.....	359.3		

The composition of the recirculated gas is the same as the waste gas given in the last column.

In the top of the kiln, this waste gas and the recirculated gas must lose enough heat in dropping in temperature from 1100°C. to 300°C. to preheat the charge to 900°C. and furnish 70% of the total radiation loss. The following table shows the fraction of the heat supply contained in the waste gas.

Gas	Mols	Heat content, C.h.u.		Difference, C.h.u.	Mols × difference, C.h.u.
		At 1100°C.	At 300°C.		
CO_2	82.6	12,500	2,920	9,580	792,000
O_2, N_2	11.0 + 247	8,000	2,070	5,930	1,529,000
H_2O	18.7	9,850	2,530	7,320	137,000
Total	359.3	.....	.....	.....	2,458,000

This is a heat loss of 2,458,000/359.3 = 6,840 C.h.u. per mol of gas. The remaining calculations may be indicated as follows:

Average specific heat of limestone, 20 to 900°C.,
0.202 + 0.0001(900 + 20)/2 = 0.248.

Heat required to preheat limestone,	C.H.U.
2,000(100.1/56.1)(0.248)(900 − 20) =	779,000
Heat loss by radiation in preheating zone and connections (70% of total radiation loss), 0.70(3,088,000) =	2,162,000
Total heat requirement	2,941,000
Furnished by waste gas	2,458,000
Furnished by recirculated gas	483,000

Mols recirculated gas, 359.3(483,000/2,458,000) = 70.6

This is, of course, the total recirculated gas including water vapor. Its volume is found to be (70.6)(359)(573/273) = 53,300 cu. ft. per hour at 1 atm., and represents

$$\frac{(70.6)(100)}{70.6 + 359.3} = 16.4\% \text{ of the total stack gas.}$$

The mols of gas passing through the charge per pound of lime produced = (70.6 + 359.3)/2,000 = 0.215.

It is now required to find the distribution ratio between primary and secondary air. The total air is known to be 20%

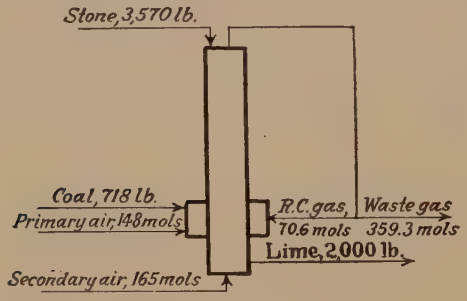


FIG. 9.—Lime kiln with Eldred-Doherty recirculation. *Basis.*—1 hr.

in excess of that theoretically required. Its amount was indicated when the fuel requirement was computed. There it was shown that 247 mols of N_2 were used. This would mean (247)(100/79) = 313 mols of air. The calculation of the amount of either the primary or secondary air will obviously give the ratio of one to the other. Insufficient data are given concerning the secondary air entering the bottom of the kiln, but the amount of

primary air entering the furnace can be determined by using a heat balance on the furnace itself, considered as dissociated from the rest of the kiln.

The heat input is the heat content of the recirculated gas plus the heat of combustion of the coal, corrected for any carbon and hydrogen not burning to CO_2 and H_2O in the furnace. It has been shown that the heat content of the waste gas above 20°C. is $97{,}900 + 934x$ for 359.3 mols, or, since x equals 718, is 767,900 C.h.u. Therefore, the heat supply of 70.6 mols is 767,900 (70.6/359.3) = 151,000 C.h.u. If the atoms of carbon burning to CO are represented by y, the mols of hydrogen present as such in the furnace gas will be $y/4$. The lower heats of combustion of CO and H_2 are 68,000 and 58,000, respectively. Consequently, the net heat of combustion of the coal is $(7{,}595)(718) - 68{,}000y - 58{,}000(y/4)$. The total heat input to the furnace is $151{,}000 + (7{,}595)(718) - 68{,}000y - (58{,}000)(y/4) = 5{,}605{,}000 - 82{,}500y$. This heat is used to heat up the reaction products, CO, H_2, H_2O and N_2 (there being no O_2), to 1100°C. and furnish 15% of the radiation loss. To compute the sensible heat in the products of combustion their amounts must first be known. Their source is recirculated gas, coal and air. The following table is based on the coal analysis and the amount and composition of the recirculated gas, and should be self-explanatory.

	Mols
Total C in gas ($CO + CO_2$), $0.0652(718) + 70.6(82.6/359.3) =$	63.0
Total H_2 in gas ($H_2O + H_2$), $0.0261(718) + 70.6(18.7/359.3) =$	22.4
C as CO	y
C as CO_2	$63.0 - y$
H_2 as H_2	$y/4$
H_2 as H_2O	$22.4 - y/4$
O_2 required, $y/2 + (63.0 - y) + (22.4 - y/4)/2 =$	$74.2 - 0.625y$
O_2 from recirculated gas, $(70.6/359.3)(82.6 + 11.0 + 18.7/2) =$	20.2
O_2 required from air (by difference)	$54.0 - 0.625y$
N_2 from air, $(54.0 - 0.625y)79/21 =$	$203.2 - 2.35y$
N_2 from recirculated gas, $70.6(247.0/359.3) =$	48.5
Total N_2	$251.7 - 2.35y$

The sum of the diatomic gases is

$$y + y/4 + 251.7 - 2.35y = 251.7 - 1.10y.$$

The sensible-heat contents of the gases are given below:

Gas	Heat content, C.h.u.		Difference = sensible heat per mol, C.h.u.
	At 1100°C.	At 20°C.	
CO_2	12,500	180	12,320
N_2, H_2, CO	8,000	140	7,860
H_2O	9,850	170	9,680

Hence, the sensible heat of the gases is

$$(63.0 - y)(12{,}320) + (251.7 - 1.10y)(7{,}860) + (22.4 - y/4)(9{,}680) = 2{,}971{,}000 - 23{,}390y \text{ C.h.u.}$$

The radiation loss is 0.15(3,088,000) = 463,000 C.h.u. Equating heat input to heat output gives an equation in y, namely,

$$5{,}605{,}000 - 82{,}500y = 2{,}971{,}000 - 23{,}390y + 463{,}000,$$

which, when solved, gives $y = 36.7$.

If the oxygen required in the form of primary air is $54.0 - 0.625y$, then the primary air is $(54.0 - 22.9)(100/21) = 148$ mols. This is 47.3% of the total of 313 mols required, whence the secondary air is 165 mols, or 52.7%.

The heat liberated by combustion of the coal in the furnace = (7,595)(718) − (68,000)(36.7) − (58,000)(36.7/4) = 2,425,000 C.h.u., which is (100)(2,425,000)/(7,595)(718) = 44.5% of the total heat of combustion of the fuel.

Knowing y to be 36.7, the composition and the amount of the furnace gas can be found:

Gas	Function	Mols	Fraction	Per cent
CO_2	$63.0 - y$	26.3	26.3/237.7	11.1
CO	y	36.7	36.7/237.7	15.4
H_2	$y/4$	9.2	9.2/237.7	3.9
N_2	$251.7 - 2.35y$	165.5	165.5/237.7	69.6
Total dry	.....	237.7	.....	100.0
H_2O	$22.4 - y/4$	13.2		
Total wet gas	.....	250.9		

As a final check on the system, the temperature to which the secondary air is preheated should be calculated. The heat taken

up by the air is equal to that given up by 2,000 lb. of lime in cooling from 900 to 250°C., or $2{,}000 \times 0.18 \times (900 - 250) = 234{,}000$ C.h.u., less the radiation loss in this zone, which is 5% of 3,088,000, or 154,000 C.h.u. There are 165 mols of secondary air to pick up this heat, 80,000 C.h.u., corresponding to 485 C.h.u. per mol. Since a mol of air has a heat content of 140 C.h.u. at 20°C., it will be heated to the temperature at which its heat content is 625 C.h.u. per mol. From the heat chart this is found to be 93°C.

The following table exhibits a comparison between the quantitative behavior of the kiln with and without the recirculation system. Compare also Figs. 8 and 9.

	Without recirculation	With recirculation
Pounds lime produced per hour	2,000	2,000
Pounds lime per pound coal	2.68	2.78
Per cent excess air	52.7%	20% (fixed)
Coal used	745 lb.	718 lb.
Mols gas through lime per pound lime	0.23 mol	0.215 mol
Per cent stack gas recirculated	0%	16.4%
Cubic feet stack gas recirculated per hour	0	53,300 cu. ft.
Per cent total heat of coal lost up stack	17%	14.1%
Per cent lower heating value of coal in sensible heat of lime	1.5%	1.5%
Per cent lower heating value of coal used to decompose lime	26.8%	27.8%
Per cent lower heating value of coal to radiation, etc	54.7%	56.6%
Per cent lower heating value of coal liberated in furnace	100%	44.5%

It can readily be seen from the results obtained that the advantages of the Eldred-Doherty recirculation system lie not in fuel saved nor in lower costs of operation, but in the higher quality and greater uniformity of the product.

Illustration 6.—The following data were obtained from a test on a rotary cement kiln, 135 ft. in length and 76 in. in outside diameter. The raw mix was fed from a storage bin through a cast-iron pipe set in the brick stack chamber. This dropped

the charge into the rear of the kiln, whence it passed down toward the fire end, the time in the kiln being about an hour and a quarter. The fuel was finely powdered coal, from 100 to 200 mesh, blown in by compressed air under from 60 to 70 lb. pressure. From the fire end of the kiln the clinker dropped into a cooler, a cylindrical steel shell lined with fire brick, similar to the kiln but smaller in size. The clinker was cooled by cold air from the room entering at the lower end of the cooler, flowing countercurrent to the clinker and feeding from the upper end into the kiln, furnishing the main air supply.

The object of the test was to determine, first, the coal consumption and raw mix required per 100 lb. of clinker produced and, second, the heat distribution.

The only weight measurement it was practicable to take was that of the cement produced; this was corrected for the gypsum added in order to get the clinker. Although the coal was weighed automatically for the entire plant of 25 kilns, some of these were 8 and some 10 ft. in diameter, with widely different production and fuel consumption, so that the amount of fuel used in the kiln in question could not be measured directly, but had to be calculated from other data obtained in the test.

It should be noted that the temperature of the flue gas is probably somewhat in error. This was measured by a thermocouple inserted in the gas, which radiated heat to the colder walls and therefore read lower than the true temperature of the gas.

DATA

Duration of test	8 hr.
Cement produced (clinker plus gypsum)	41,260 lb.
Gypsum added	1,280 lb.
Clinker produced, net	39,980 lb.
Temperatures:	
Clinker falling from kiln	2424°F.
Maximum kiln temperature	2767°F.
Clinker leaving cooler	1100°F.
Flue gases	1411°F.
Entering air:	
Wet bulb	23.6°F.
Dry bulb	27.6°F.
Barometer	29.9 in.
Anemometer, point of air entrance to cooler	244 ft. per min.

	Per Cent
Average flue-gas analysis:	
CO_2	25.39
O_2	0.89
CO	0.08
N_2	73.64
Clinker analysis:	
CaO	63.42
MgO	3.28
Fe_2O_3, Al_2O_3	11.42
SiO_2	20.80
SO_3	0.63
Raw-mix analysis:	
CO_2	33.34
CaO	41.97
SiO_2	13.00
Fe_2O_3, Al_2O_3	7.00
MgO	2.50
Graphite	0.65
FeS_2	0.56
H_2O	0.71
Coal analysis:	
C	64.59
H	5.07
S	1.76
N	1.71
O	5.97
Moisture	0.86
Ash	20.04
Heat of combustion, 12,160 B.t.u.	

Solution.—There are three streams of materials entering the kiln: air, coal and raw mix; and two leaving it: clinker and stack gas. Thus the problem involves the relation of these five quantities. By a nitrogen balance, however, the air used is a direct function of the gas evolved, thus reducing the quantities to four. If one of these is made the basis of calculation, three are left as unknowns. Let the basis of calculation be 100 lb. of clinker and the unknowns:

x = the pounds of coal per 100 lb. of clinker.
y = the pounds of raw mix per 100 lb. of clinker.
z = the mols of dry stack gas per 100 lb. of clinker.

Assume that all the ash from the coal enters the clinker and neglect the difference in composition between the clinker and the

burnt portion of the stack dust. It is true that the alkalies concentrate in the stack dust due to volatilization; but, as will immediately appear, the ratios of raw mix, coal and stack gas to clinker are computed by balances involving other elements than the alkalies and, since the amount of dust is not large and the percentages of these other elements in it do not differ greatly from those in the clinker, the error due to dust is slight. It does, however, follow that the term *100 lb. of clinker* used as a basis is the sum of the clinker actually discharged from the firing end of the kiln plus the corresponding amount of burnt clinker going up the stack as dust. Any unburnt raw mix going up the stack as part of the total dust does not appear in the computations or affect them in any way.

To determine these three values, three equations will be necessary. The first of these will be an oxygen balance, the second a carbon balance and the third an equation of input to output of non-volatile oxides.

Before setting up the actual equations, the various analyses should be reevaluated in order to arrive more readily at the proper figures to be used.

Basis.—100 mols of dry stack gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	25.39	25.39	25.39
O_2	0.89	.....	0.89
CO	0.08	0.08	0.04
N_2	73.64		
Total	100.00	25.47	26.32

Basis.—100 lb. of clinker.

	Pounds
CaO	63.42
MgO	3.28
Fe_2O_3, Al_2O_3	11.42
SiO_2	20.80
Non-volatile oxides	98.92
SO_3	0.63

Basis.—100 lb. raw mix.

	Pounds	Non-volatile oxides	Atoms C
CO_2	33.34	.....	0.758
CaO	41.97	41.97	
SiO_2	13.00	13.00	
Fe_2O_3, Al_2O_3	7.00	7.00	
MgO	2.50	2.50	
Graphite	0.65	.....	0.054
FeS_2	0.56	0.37(Fe_2O_3)	
H_2O	0.71		
Total	.....	64.84	0.812

Basis.—100 lb. coal.

	Pounds	Mols or atoms
C	64.59	5.38
H_2	5.07	2.51
S	1.76	0.05
N	1.71	
O	5.97	0.37
Moisture	0.86	0.05
Ash	20.04	
Net H_2, 2.51 − 0.37 =	.....	2.14

Although there is some sulfur in both the coal and the raw mix, it is assumed that the stack gases contained none, since it is largely absorbed as sulfate by the lime and alkalies in the clinker and stack dust. Since the analysis of the clinker shows that over half the sulfur from the pyrites was converted to SO_3 and since the amount of FeS_2 present is small, little error will be introduced by assuming complete combustion to SO_3 by the reaction,

$$4FeS_2 + 15O_2 = 2Fe_2O_3 + 8SO_3.$$

Therefore, 15 mols of oxygen are required for every 4 mols of FeS_2. Likewise, the sulfur in the coal will be considered as oxidized to SO_3.

For the oxygen balance, the following equality must hold: (O_2 from air) + (O_2 from raw mix) = (O_2 in stack gas) + (O_2 for net H_2 in coal) + (O_2 for S in coal) + (O_2 for FeS_2 in raw mix). In this equation O_2 means only that oxygen which affects

or is affected by the dry stack gas. Thus, combined water and moisture in the coal do not enter into account, nor does the oxygen in the form of the non-volatile oxides, such as CaO, MgO, Al_2O_3, etc., come into consideration; yet the oxygen in the form of CO_2 in the carbonates in the raw mix must be allowed for, since it passes into the stack gases. Using the values obtained in the tabulated analyses and employing mols throughout, the oxygen balance becomes

$$0.7364z(21/79) + 0.00758y = 0.2632z + 0.0214x/2 + 0.0005x(3/2) + (0.0056/120)(15/4)y.$$

Upon simplification this reduces to

$$0.00740y - 0.0115x = 0.0674z.$$

Similarly, setting up the carbon balance—(C from coal) + (C from raw mix) = (C in stack gas)—gives the following equation:

$$0.0538x + 0.00812y = 0.2547z.$$

The equation for the non-volatile oxides is: Oxides from raw mix + Ash from coal = Oxides in clinker, giving

$$0.6484y + 0.2004x = 98.92.$$

Solution of these three equations gives the following values:

x = 29.3 lb. of coal.
y = 143.5 lb. of raw mix.
z = 10.75 mols of stack gas.

Based upon the original analyses and the assumptions regarding the combustion of sulfur and pyrites in the raw materials, the above values represent a rigidly correct solution of the problem. The use of an equation involving the sum of all the non-volatile oxides is new, since heretofore balances containing only a single element or oxide rather than a group of elements have been employed. Furthermore, a direct solution based on any one non-volatile component is impossible, since the analysis of the coal ash was not made. It will be noted, however, that, in the non-volatile oxide balance, the term "ash from coal" is small compared with the other two terms. Hence, although an error in the ash or its composition will produce the same numerical error in the other terms, the *percentage* error will be very much less. If, now, the composition of this ash can be assumed to be 10% CaO, 45% SiO_2 and 45% $Al_2O_3 + Fe_2O_3$, lime, silica and

alumina plus iron balances can be written for the kiln. Equating the lime input in the coal and raw mix to the output in the clinker,

$$(0.10)(0.2004)x + 0.4197y = 63.42. \quad (1)$$

Similarly for the SiO_2,

$$(0.45)(0.2004)x + 0.1300y = 20.80, \quad (2)$$

and for $Al_2O_3 + Fe_2O_3$,

$$(0.45)(0.2004)x + 0.0700y = 11.42. \quad (3)$$

Combining and solving, Eqs. (1) and (2) give for y, 150; Eqs. (2) and (3) give for y, 156; and Eqs. (1) and (3), 150. The solutions involving a lime balance are probably most accurate, whence, using this approximate method, the value 150 would be assumed correct. This differs by 4.5% from the value 143.5 previously found.

The value of x must not be determined from these last three equations, since the quantities containing x as a factor have been estimated. As before, the relation between the coal on the one hand and the clinker and the raw mix on the other can be determined accurately only through the stack gas. Using the equations for oxygen and carbon balances already worked out and inserting the value 150 for y, the following result is obtained:

$$0.00740(150) - 0.0115x = 0.0674z, \text{ and}$$
$$0.0538x + 0.00812(150) = 0.2547z.$$

Solution of this pair of equations gives 30.7 for x and 11.25 for z.

This approximate solution serves to indicate with what precision values may be obtained when based upon an assumption such as the above. In the following calculations on the heat balance, the results obtained by the more rigid method will be used.

Heat Balance

Normally, a heat balance is based upon the temperature of the surroundings, but in this case 32°F. will be taken as a base line, partly for convenience (since the heat chart available is based on this temperature and does not go below it) and partly to emphasize the fact that any reference point desired may be employed. Furthermore, although in furnace practice the heat balance is most frequently based on the higher heating value of the fuel as directly determined in a bomb or Junker's calorimeter (therefore including the heat of condensation of all water resulting from the combustion of the fuel), in this case the lower

heating value will be employed. The use of the higher heating value is, in a very definite sense, illogical, because industrial furnaces are almost never in a position to recover this heat of vaporization of the water from the fuel, and hence to charge them with it in reporting their efficiency tends to give a distorted impression of their performance.

The heat balance will be that of the cooler and kiln combined. Here also the basis of calculation will be 100 lb. of clinker.

Heat Input.—Heat of combustion of coal,

$$29.3(12{,}160) = 356{,}000 \text{ B.t.u.}$$

Heat of vaporization of water formed on combustion,

$$29.3(0.0251 + 0.0005)(18)(1{,}073) = 14{,}500 \text{ B.t.u.}$$

The value 1,073, taken from the steam tables, is the heat of vaporization of water at 32°F. in B.t.u. per pound.

Net heat input from coal, 356,000 − 14,500 = 341,500 B.t.u.

Graphite has a heat of combustion of 94,800 C.h.u. per atom of carbon, and the heat of combustion of FeS_2, when burning to Fe_2O_3 and SO_3, is 246,100 C.h.u. per mol. The heat input due to the presence of these two substances in the raw mix would, therefore, be

$$143.5[0.00054(94{,}800) + (0.0056/120)246{,}100]1.8 = 16{,}300 \text{ B.t.u.}$$

Adding this to the 341,500 B.t.u. already calculated gives 357,800 B.t.u. as the total heat input.

Heat Output.—1. *Heat of reaction.* Among the reactions which may take place in the kiln are the following:

$$CaCO_3 = CaO + CO_2 - 42{,}500 \text{ C.h.u.}$$
$$MgCO_3 = MgO + CO_2 - 28{,}900 \text{ C.h.u.}$$
$$CaO + SiO_2 = CaSiO_3 + 17{,}400 \text{ C.h.u.}$$
$$2CaO + SiO_2 = Ca_2SiO_4 + 28{,}400 \text{ C.h.u.}$$
$$Al_2O_3 + SiO_2 = Al_2SiO_5 - 12{,}000 \text{ C.h.u.}$$
$$Al_2O_3 + 2SiO_2 = Al_2Si_2O_7 + 14{,}900 \text{ C.h.u.}$$
$$CaO + Al_2O_3 = CaAl_2O_4 + 3{,}400 \text{ C.h.u.}$$

Regarding these reactions and the analyses of the raw mix and clinker, the following assumptions will be made:

All the MgO in the raw mix is in the form of $MgCO_3$.
The rest of the carbonate in the raw mix is $CaCO_3$.
Any CaO not present as carbonate is present as $CaSiO_3$.
The CaO in the ash from the coal is in the form of $CaSiO_3$.

The amount of the ash is small and this last assumption is of relatively little importance.

Part of the CaO in the clinker is present as Ca_2SiO_4, part as Ca_3SiO_5 and the rest as $Ca_2Al_2O_5$ and $Ca_3Al_2O_6$. The thermochemical equations show that the addition of 1 mol of CaO to 1 mol of SiO_2 evolves 17,400 C.h.u. and of 2 mols of CaO to 1 mol of SiO_2 an additional 11,000 C.h.u., or a total of 28,400 C.h.u. It is well known that successive additions of base to a polybasic acid generate progressively decreasing amounts of heat for each equivalent of base added, and where three equivalents may be added the heat effect corresponding to the third is nearly negligible. Thus, it may be assumed that the heat of formation of tricalcium silicate is also 28,400 C.h.u., *i.e.*, the heat of addition of lime to $CaSiO_3$ may be taken as 11,000 C.h.u. per mol of silicate, independently of the amount of lime added.

In the analysis of both the clinker and raw mix, the Al_2O_3 is reported with the Fe_2O_3. Although this is largely Al_2O_3, it is not known whether it is combined with 1 or 2 mols of SiO_2 per mol of Al_2O_3. In any case the heat of one reaction is positive and of the other negative, so that the heat of decomposition of the aluminum silicates is small. Likewise, the amounts finally present as $Ca_2Al_2O_5$ or as $Ca_3Al_2O_6$ cannot be determined, but here again the data indicate that the heat of formation of calcium aluminates is also small. It will be assumed that these two offset each other, *i.e.*, the net heat effect of the two is practically zero.

Basis.—100 lb. clinker.

From raw mix:	
Mols CO_2 = 0.758(1.435) =	1.088
Mols MgO = 0.062(1.435) =	0.089
Mols CaO as $CaCO_3$ =	0.999
Total mols CaO = 0.750(1.435) =	1.076
Mols as $CaSiO_3$	0.077
Mols SiO_2 = 0.216(1.435) =	0.310
	0.233
From clinker:	
Total CaO, 63.42/56 =	1.131
Total SiO_2, 20.80/60.1 =	0.346
CaO from coal, 1.131 − 1.076 =	0.055
SiO_2 from coal, 0.346 − 0.310 =	0.036

The values of CaO and SiO_2 from the coal are obtained by differences of relatively large quantities, but are near enough to

justify the original assumption that the lime and silica were combined as $CaSiO_3$ in the coal ash. Of the total SiO_2, 0.346 mol, 0.077 + 0.036 = 0.113 mol is already combined as $CaSiO_3$; the rest, 0.233 mol, is either as free silica or combined with alumina. Using these figures and the heats of formation, the heats of reaction may be calculated.

1. Heat absorbed.

	C.H.U.
Decomposition of $MgCO_3$: 0.089(28,900) =	2,570
Decomposition of $CaCO_3$: 0.999(42,500) =	42,460
Total absorbed =	45,030

2. Heat evolved.

Addition of CaO to $CaSiO_3$: 0.113(11,000) =	1,240
Reaction of SiO_2 with CaO: 0.233(28,400) =	6,620
Total evolved =	7,860

3. Heat of reaction.

(1) − (2), 45,030 − 7,860 =	37,170
(37,170)1.8 =	66,900 B.t.u.

It is recognized that this result is somewhat arbitrary. In the absence of complete analyses and adequate thermochemical data, this must necessarily be so. However, the heats of reaction of those substances present in large amount have been calculated and the final figure is reasonably accurate.

2. *Sensible heat content of gases.*

Basis.—100 mols dry stack gas.

Water vapor from air (pressure H_2O = 2 mm.):

Mols N_2	Mols air	
73.64	100	2
	79	758

= 0.246 mol H_2O

Water vapor from charge:

Mols gas	Pounds charge	Pounds H_2O	
100	143.5	0.0071	
	10.75		18

= 0.526 mol H_2O

Water vapor from combustion of coal:

Mols gas	Pounds coal	
100	29.3	(2.51 + 0.05)
	10.75	

= 6.99 mols H_2O

Total water vapor, 0.246 + 0.526 + 6.99 = 7.76 mols.

Sensible heat content above 32°F.:

Gas	Mols	Heat content, B.t.u. at 1411°F.	Mols times heat content
CO_2	25.39	15,000	381,000
CO, O_2, N_2	74.61	10,000	746,000
H_2O	7.76	12,200	95,000
			1,222,000

Basis.—100 lb. clinker.

$$10.75(1{,}222{,}000/100) = 131{,}500 \text{ B.t.u.}$$

3. *Potential heat in gas due to CO.*

$$10.75(0.0008)(68{,}000)1.8 = 1{,}052 \text{ B.t.u.}$$

4. *Sensible heat in clinker.*—Assume 0.25 as its average specific heat.

$$100(0.25)(1{,}100 - 32) = 26{,}700 \text{ B.t.u.}$$

5. *Heat required to bring charge, coal and air to 32°F.*—Assume 0.20 as the specific heat of the solids and use 6.7 as the molal heat capacity of air.

B.t.u.

$(143.5 + 29.3)(0.20)(32 - 27.6) =$ 152

Mols gas	Mols N_2	Mols dry air	Mols air	B.t.u. per deg.			
10.75	73.64	100	760	6.7	(32 − 27.6)	=	297
	100	79	758			Total.....	449

6. *Heat of vaporization at 32°F. of water in charge.*

$$(143.5)(0.0071)(1{,}073) = 1{,}093 \text{ B.t.u.}$$

SUMMARY OF HEAT DISTRIBUTION

	B.t.u.	Per cent
Heat input	357,800	100.0
Heat output:		
Heat of reaction	66,900	18.7
Sensible heat in gas	131,500	36.7
Potential heat in gas	1,052	0.3
Sensible heat in clinker	26,700	7.5
Heat required for charge	449	0.1
Heat to vaporize water in charge	1,093	0.3
Heat loss, by difference	130,106	36.4
Heat output = Heat input	357,800	100.0

PROBLEMS

1. A limestone containing, on the dry basis, 45% CO_2 and no other volatile matter is burnt with a coal containing 74.8% C, 5.7% H, 9.8% ash, 1% N, negligible S and 8.7% O. The analysis of the stack gas is 25.3% CO_2, 3.8% O_2 and 70.9% N_2. The stack gases leave at 500°F. and 760 mm. The air is dry. Calculate:

(*a*) Pounds of lime produced per pound of coal. *Ans.* 3.30.

(*b*) Per cent of excess air. *Ans.* 25.2%.

(*c*) Cubic feet of stack gas per ton of lime. *Ans.* 217,300.

2. The gases from a shaft lime kiln externally fired are 20% CO_2, 5.2% O_2 and 74.8% N_2, and leave the kiln at 390°F. The coal used has a heating value of 13,060 B.t.u. per pound, and its analysis is 77% C, 6% H, 1.2% N, 1.1% S, 7.5% ash and 7.2% O. The limestone contains 81% $CaCO_3$, 6% $MgCO_3$, 10.5% inert and 2.5% moisture. The air enters at 70°F. with a vapor pressure of water of 12.2 mm., the barometric pressure being 758 mm. The lime leaves the kiln at 508°F.

The heat of formation of $MgCO_3$ from MgO and CO_2 at 70°F. is 26,300 g. cal. per gram mol. The specific heat of the burnt lime is 0.18. Calculate:

(*a*) The fuel ratio, *i.e.*, the pounds of burnt lime produced per pound of coal. *Ans.* 2.67.

(*b*) Per cent of excess air. *Ans.* 35.4%.

The heat distribution in the kiln, expressed as per cent of the heating value of the coal burnt, composed of the following items:

(*c*) Sensible heat in the waste gases. *Ans.* 10.45%.

(*d*) Latent heat in the waste gases. *Ans.* 6.43%.

(*e*) Heat of decomposition of lime. *Ans.* 23.19%.

(*f*) Sensible heat in the lime. *Ans.* 1.67%.

(*g*) "Radiation and unaccounted-for" loss. *Ans.* 58.26%.

3. An Eldred-Doherty lime kiln, burning a very pure limestone containing on the dry basis 2.0% SiO_2, Al_2O_3, Fe_2O_3, etc. and only a trace of magnesia, uses a coal of the following ultimate analysis: 3.8% moisture, 67.2% C, 5.3% H, 3.2% S (mainly as pyrites), 0.8% N and 11.4% ash. The gases going to the stack are 26.9% CO_2, 2.8% O_2 and no CO. It is desired to determine what per cent of the total gases leaving the top of the kiln are recirculated. This is done by carefully sampling and analyzing the gases passing over the fire-bridge wall from the furnace, and they are found to contain 0.4% SO_2, 14.2% CO_2, 13.9% CO, no O_2, 1.1% illuminants (C_2H_4), 0.7% CH_4 and 3.7% H_2. Calculate:

(*a*) The per cent of the kiln gases recirculated. *Ans.* 19.1%.

(*b*) Pounds of lime produced in this kiln per pound of fuel burnt. *Ans.* 3.50.

(*c*) The per cent of the total air used which was admitted to the fire box. *Ans.* 35.4%.

4. It is desired to determine the fuel consumption per barrel (380 lb.) of cement clinker discharged from a certain rotary kiln, neglecting any dust going up the flue. The powdered coal employed comes, however, from grinding equipment which also serves several other kilns, and on account of this difficulty and fire risk it is deemed inadvisable to attempt to isolate the

fuel of this kiln for weighing. Calculate the desired figure from the following analytical data, the first three analyses coming from the control laboratory, and the rest of the data being obtained for this particular purpose:

Cement rock	Per cent	Limestone	Per cent	Coal	Per cent
SiO_2.....	22.22	SiO_2.....	0.92	C.....	79.77
Al_2O_3.....	7.25	Al_2O_3.....	0.48	H.....	4.65
Fe_2O_3.....	0.92	CaO.....	54.60	S.....	0.52
CaO.....	35.53	MgO.....	0.53	N.....	1.83
MgO.....	2.19	CO_2.....	43.47	O.....	4.59
CO_2.....	30.29	Alkalies, etc...	Trace	Ash.....	8.64
Alkalies, etc...	1.60				

The cement rock and limestone are mixed and ground in the ratio of 100:32 by weight. The air for combustion is at 16°C., and 37% saturated. The barometer is 750 mm. The analysis of the flue gases is 27.4% CO_2, 0.4% CO, 1.2% O_2 and 71.0% N_2. The flue gases have a dew point of 35°C. *Ans.* By carbon balance, 80.1 assuming no loss of alkalies or 81.5 assuming complete volatilization; by hydrogen balance, 78.2 or 79.7.

CHAPTER VI

STOICHIOMETRY OF FURNACE AND KILN DESIGN

This is obviously not the place for a detailed discussion of furnace design, involving as that does the chemistry of combustion, flow of fluids, transmission of heat by both radiation and conduction, the complicated chemical relationships of the particular reactions for which the furnace is built, the choice of suitable refractories, proper mechanical construction, provision for insulation, ease and accuracy of operating control, labor-saving devices and the like. For any such design, however, the first step which must be taken is the solution of the stoichiometric problems involved.

In every problem of design certain conditions are fixed by the very nature of the case. Thus, in designing a furnace for the production of nitric acid, it is necessary to give the capacity which the furnace must have, the allowable excess of decomposing acid which may be used, but must not be exceeded, the maximum allowable rate of evolution of the gases and the like. On the other hand, the designing engineer himself would make certain assumptions. These assumptions are frequently equivalent to setting up an ideal which may or may not be possible of actual realization. The designer must base his computations on both fixed conditions and assumptions, checking his quantitative conclusions with the greatest care to make sure that the final design is a consistent one. In the solution of complicated problems of this sort, one or more of the assumptions are almost always found incompatible with the others. In such cases the assumptions must be revised and the design modified accordingly. The methods of stoichiometry are invaluable for the elimination of errors by cross-checking of this sort.

It is obvious that, to a greater or less degree, such computations involve methods of trial and successive approximations. General rules of procedure are difficult to give. It will probably be most helpful to discuss a specific case.

Assume that it be required to design a gas-fired tunnel kiln, operated continuously, for the burning of a ceramic material

which passes through the tunnel in a direction countercurrent to that of the gases. The stock enters one end of the tunnel and in passing toward the middle is preheated by the sensible heat of the hot products of combustion flowing in the opposite direction. This end will be called the preheating zone. These combustion products go to the stack at that end of the tunnel where the stock enters. Combustion itself takes place in the middle of the tunnel (combustion zone) where the stock is heated to the maximum temperature of burning. The stock now passes out the opposite end of the tunnel (cooling zone), in which it is cooled partly by means of the air necessary for combustion and partly by conduction and radiation through and from the walls. This air is preheated, thereby conserving heat in the operation of the furnace. The stock goes through the tunnel on cars, the lower part constructed of steel and cast iron and the upper of refractory. On these cars is placed the charge. One of these cars is pushed into the furnace every 4 hr., pushing out a similar car at the other end. The firing of the furnace is continuous. The number of cars in the furnace is so large that no serious error will be made in assuming that the movement of the stock is also continuous. The metal of each car weighs 1,000 lb., the refractory 2,000 lb. and the charge 6,000 lb. The stock has been carefully dried before it comes to the furnace. The specific heat of the refractory may be taken as $0.20 + 0.0001t$ and that of the charge as $0.22 + 0.00012t$, t being in degrees Centigrade. In the range from 600 to 700°C., the charge loses its combined water, of which it contains 6.2%. The heat of decomposition of the clay with evolution of this water, expressed per gram mol of water lost, is estimated to be 15 kg.-cal. After this decomposition the specific heat of the charge may be taken as that of the refractory given above. Stock, air and gas enter the furnace at 20°C. The stock must be burnt to 1210°C., and the temperature rise and fall must be substantially uniform.

The burning schedule demanded by the characteristics of the stock involves 200 hr. in the kiln. Since the cars are 6 ft. long, this requires a furnace length of 300 ft., of which 150 ft. must be in the preheating zone, 15 ft. in the combustion and 135 ft. in the cooling zone.

The preceding may be taken as the fixed conditions which, in any case, the furnace must be designed to meet. These are not subject to alteration. On the other hand, it is very desirable to

cool the stock to at least 160°C., before it leaves the furnace and to preheat it before it enters the combustion zone to 1110°C. Furthermore, while such a furnace will be carefully insulated against loss of heat, its surface area is so large that the heat lost by conduction and radiation through the walls is sure to be considerable. Obviously, the insulation should be more or less proportioned to the temperature of the furnace at the point in question, *i.e.*, in a well-designed furnace the heat loss per unit length will be substantially constant. For the conditions under which this furnace is to operate, it is claimed that it will not pay to try to insulate sufficiently to reduce the heat loss per foot of length below 9,000 B.t.u. per hour in the preheating and combustion zones and 80% of this in the cooling zone. The loss in the latter is less because the gases and hence also the kiln walls are cooler than the stock, rather than hotter as in the rest of the furnace. It will probably be inadvisable to try to cool the stack gases below 240°C., or to preheat the air above 1000°C. The metal of the cars and the lower part of the refractory base are protected from the full heat of the kiln. Failure of the refractory to come up to temperature is more or less counterbalanced by heat picked up by the metal. Consider this counterbalancing exact, *i.e.*, assume all the refractory brought to full temperature but the metal not heated at all. These figures represent the tentative assumptions on which to attempt a furnace design.

It is required to design such a kiln, using as fuel a natural gas, which may be assumed substantially CH_4. It is further desired to modify the design so that the furnace can replace this fuel with producer gas of the following composition: 7% CO_2, 21% CO, 15% H_2, 1% CH_4 and 56% N_2. Finally, the fuel saving which can be realized by an increase in insulation sufficient to halve the heat loss by conduction and radiation is to be estimated.

Solution.—Since in the preheating zone the stock must rise in temperature at a substantially uniform rate, $(1{,}110 - 20)/150 = 7.27°$ per foot of travel, and since the heat capacity of the stock does not change greatly with the temperature, it follows that the B.t.u. consumption per foot of length of kiln for heating the stock is nearly constant throughout this zone, although this neglects the temperature effect of dehydration. As has already been explained, the kiln is to be constructed so that the same is true of the heat loss by conduction and radiation. Since the

heat supply of any particular foot of length of the preheating zone comes solely from cooling the gases, and since the gases passing any particular section per unit of time are the same as those at any other section, neglecting the slight change of heat capacity with the temperature, it follows that the fall in temperature of the gases per unit length is constant throughout this zone. Since the rate of heating of the stock must be uniform and this rate of heating is proportional to temperature difference between gas and stock, this latter should be kept substantially constant. Therefore, assume that the temperature difference between the gas and stock at the two ends of the preheating zone is the same, *i.e.*, 220°C.

Study of the problem shows that this furnace consists of three separate sections, namely, the preheating, combustion and cooling zones. Obviously, a heat balance can be set up for each of these zones and such a heat balance will give information regarding the operation of the furnace which is absolutely dependable. The relationships existing in the cooling zone are less complicated than those in the other two. It is, therefore, advisable to set up first a heat balance for this zone.

The heat supply to this part of the furnace comes solely from the sensible heat of the burnt stock which enters this zone at 1210°C. and cools to 160°C. The average temperature of the stock in this zone is, therefore, $(1{,}210 + 160)/2 = 685$°C. At this temperature the specific heat of the stock from the formula, $0.20 + 0.0001t$, is 0.2685. This figure is the average specific heat of the stock between the temperature limits quoted because its specific heat is linear with the temperature. The heat given up by the stock is, therefore, its weight times its temperature drop times this specific heat. In burning, the 6,000 lb. of stock on each car lose 6.2% of water, leaving a burnt stock weight of 5,630 lb. Adding the weight of the refractory base of the car gives a car weight of 7,630 lb. Therefore, the heat supplied to this zone is $(7{,}630)(1{,}210 - 160)(0.2685) = 2{,}150{,}000$ C.h.u. per car or one-fourth of this, namely, 537,500 C.h.u. per hour.

The radiation loss is $9{,}000(0.8)(135)/1.8 = 540{,}000$ C.h.u. per hour. This shows the heat loss by radiation to be greater than the heat supplied to the cooling zone, absolutely no heat being available for preheating the air. There is obviously something wrong with the assumptions. The error lies in the fact that the radiation loss assumed is excessive. If a kiln were to be con-

structed with this radiation loss, the stock would be cooled by radiation alone in less than 135 ft. Since the firing schedule demands that the stock be not cooled more quickly than this, it of necessity follows that the radiation loss must be reduced, at least in the cooling zone.

The difference between the radiation loss and the sensible heat in the stock is so small that such a kiln could be built and operated successfully by the use of a very slightly increased amount of insulation, provided no air whatever be drawn through the cooling zone but only cold air be supplied at the burners. However, it seems scarcely wise to construct the kiln in this way. It is, therefore, better to increase the insulation somewhat more and reduce the heat loss through the walls, so that the air passing through the cooling zone will pick up and usefully recover the excess heat. In order to get a line on the extent to which it is advisable to carry this increased insulation, the problem will be solved, assuming first a heat loss in the preheating and combustion zones of 8,000 B.t.u. per hour per foot of length and, second, a figure of 4,000. The loss in the cooling zone will, as before, be 80% of that in the other two zones. Repeating the computation just made, based on the heat balance in the cooling zone, for a heat loss of 8,000 B.t.u. per hour per foot of length, the heat lost through the walls is 480,000 C.h.u. per hour and the heat usefully picked up by the incoming air is 57,500 C.h.u. per hour, while for one-half this wall loss (4,000 B.t.u. per foot of length per hour) the total wall loss in the cooling zone is 240,000 C.h.u. per hour and the heat picked up by the incoming air is 297,500 C.h.u. Multiplied by 1.8 the figures would be in B.t.u. per hour.

When an attempt is made to set up a heat balance on either the combustion zone or the preheating zone, the fact must be faced that there are two unknown quantities: the amount of gas used by the kiln and the amount of excess air employed. Since, however, two heat balances can be set up, it is possible to formulate two independent equations, one for each zone, and therefore to solve for the two unknowns. Call the mols of gas per hour x, and the mols of *excess* air y, and take 20°C. as the reference temperature. The equation for the heat balance in the combustion zone may be worded as follows:

Sensible heat recovered by preheating air in cooling zone + heat of combustion of x mols of natural gas = sensible-heat content of theoretical products of combustion above 20°C. + sensi-

ble-heat content of excess air above 20°C. + heat consumed in heating stock and car from 1110 to 1210°C. + wall loss in this section. Using the lower heating value for methane (see p. 14), the heat input is, therefore, $57{,}500 + 191{,}000x$, assuming for the time being that the radiation loss in this zone is 8,000 B.t.u. per foot of length per hour.

If, as stated above, the gas and stock maintain a substantially constant temperature difference of 220°C., the gas leaving the combustion zone must have a temperature of 1330°C., since the stock has been preheated at this point to 1110°C. From the equation, $CH_4 + 2O_2 = CO_2 + 2H_2O$, there will be x mols CO_2, $2x$ mols H_2O and $2x(79/21) = 7.52x$ mols N_2 as the theoretical products of combustion of x mols of methane, and to this must be added y mols of excess air. The sensible-heat content of these gases above 20°C. is most easily calculated by using the heat chart (Fig. 1, p. 5).

	Heat content, C.h.u.		Difference = heat gained per mol, C.h.u.
	At 1330°C.	At 20°C.	
CO_2	15,400	180	15,220
H_2O	12,100	170	11,930
N_2, O_2	10,000	140	9,860

The sensible heat in the theoretical gases of combustion is the product of the number of mols of each gas into the difference in heat content of that gas between the two temperatures, *viz.*,

$$15{,}220x + 11{,}930(2x) + 9{,}860(7.52x) = 113{,}250x,$$

and similarly for the excess air, $9{,}860\,y$.

As above, the average specific heat of the stock and car between 1110 and 1210°C. is $0.20 + 0.0001(1{,}110 + 1{,}210)/2 = 0.316$ and the heat supplied to the material,

$$(7{,}630/4)(1{,}210 - 1{,}110)0.316 = 60{,}250 \text{ C.h.u. per hour.}$$

The remaining item in the heat output in the combustion zone is the radiation loss,

$$(8{,}000/1.8)15 = 66{,}700 \text{ C.h.u. per hour.}$$

Now setting up the equation for the heat balance in this zone, there is obtained the following expression:

$$57{,}500 + 191{,}000x = 113{,}250x + 9{,}860y + 60{,}250 + 66{,}700.$$

When the radiation loss is assumed to be only 4,000 B.t.u. per hour per foot length, the heat recovered per hour in the cooling zone is 297,500 instead of 57,500 C.h.u., and the heat loss by radiation in the combustion zone is only one-half of 66,700, or 33,350 C.h.u. Hence, another equation may be written for this case, using x' as the number of mols of gas burnt and y' the mols of excess air used per hour, giving

$$297{,}500 + 191{,}000x' = 113{,}250x' + 9{,}860y' + 60{,}250 + 33{,}350.$$

In order to solve these equations, a second set is obtained from the the preheating zone. In this zone the sole source of heat supply is that contained as sensible heat in the hot gases. These are cooled from 1330 to 240°C. The number of mols of the individual gases has already been calculated, and the heat contents are again obtained from Fig. 1.

	Heat content, C.h.u.		Difference = heat loss per mol, C.h.u.
	At 1330°C.	At 240°C.	
CO_2	15,400	2,300	13,100
H_2O	12,100	2,080	10,020
N_2, O_2	10,000	1,640	8,360

This gives as the heat input

$$13{,}100x + 10{,}020(2x) + 8{,}360(7.52x) + 8{,}360y = 96{,}000x + 8{,}360y$$

The heat output consists of that necessary to heat the stock and car from 20 to 1110°C. and the radiation loss. Although the stock loses its combined water over the range from 600 to 700°C., it is assumed for the purpose of calculating the heat utilized in this zone that this occurs at 650°C. The original stock must be heated to this temperature, decomposition taking place at this point and the dehydrated material then heating up to 1110°C. Average specific heat of stock, 20 to 650°C.,

$$0.22 + 0.00012(650 + 20)/2 = 0.26.$$

Heat absorbed by stock (1,500 lb.) per hour, 20 to 650°C.

$$1{,}500(650 - 20)0.26 = 246{,}000 \text{ C.h.u.}$$

Heat of decomposition: This is estimated to be 15 kg.-cal. (15,000 g.-cal.) per gram mol of water contained, which is equivalent to 15,000 C.h.u. per pound mol of water.

Pounds stock	Pounds combined H_2O	Mols H_2O		
1,500	0.062		15,000	= 77,500 C.h.u.
		18		

Average specific heat of stock, 650 to 1110°C.,

$$0.20 + 0.0001(1{,}110 + 650)/2 = 0.288.$$

Heat absorbed by dehydrated stock, 650 to 1110°C.,

$$0.938(1{,}500)(1{,}110 - 650)0.288 = 186{,}500 \text{ C.h.u.}$$

There is also a small amount of heat recovered. The combined water, which is evolved at 650°C., mixes with the gases of combustion and is cooled with them to 240°C. Its heat content at 650°C. per mol is 4,640 C.h.u. and at 240°C., 2,080 C.h.u., the heat recovered being

Pounds stock	Pounds H_2O	Mols H_2O		
1,500	0.062		(4,640 − 2,080)	= 13,200 C.h.u.
		18		

Average specific heat of refractory, 20 to 1110°C.,

$$0.20 + 0.0001(1{,}110 + 20)/2 = 0.2565.$$

Heat absorbed by refractory (500 lb.) per hour, 20 to 1110°C.,

$$500(1{,}110 - 20)0.2565 = 139{,}700 \text{ C.h.u.}$$

	C.H.U.
Heat absorbed by stock, 20 to 650°C.	246,000
Heat of decomposition	77,500
Heat absorbed by stock, 650 to 1110°C	186,500
Heat absorbed by refractory, 20 to 1110°C	139,700
Total heat absorbed	649,700
Heat recovered by cooling water vapor	13,200
Net heat absorbed by stock and car	636,500

The radiation loss in this zone, using 8,000 B.t.u. as the loss per hour per foot length, is

$$(8{,}000/1.8)150 = 666{,}700 \text{ C.h.u.}$$

and 333,300 when the loss is half this value.

The equation for the heat balance in this zone may now be written

$$96{,}000x + 8{,}360y = 636{,}500 + 666{,}700,$$

for the first case (8,000 B.t.u. loss per hour per foot of length) and

$$96{,}000x' + 8{,}360y' = 636{,}500 + 333{,}300,$$

for the second case (4,000 B.t.u. loss per hour per foot of length).

Solving the simultaneous equations,

$57{,}500 + 191{,}000x = 113{,}250x + 9{,}860y + 60{,}250 + 66{,}700$ and $96{,}000x + 8{,}360y = 636{,}500 + 666{,}700$, the result will be:

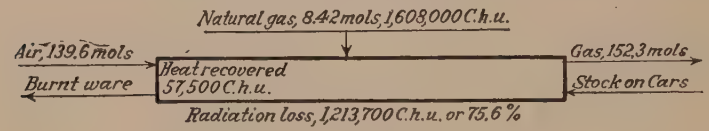
$$x = 8.42,\ y = 59.3.$$

For the equations,

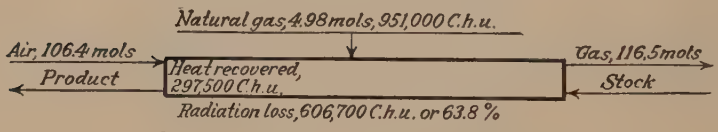
$297{,}500 + 191{,}000x' = 113{,}250x' + 9{,}860y' + 60{,}250 + 33{,}350$ and $96{,}000x' + 8{,}360y' = 636{,}500 + 333{,}300$,

$$x' = 4.98,\ y' = 58.9.$$

In order to interpret these results, consider the first case with high radiation loss. To burn 8.42 mols of CH_4 requires twice



a. 8,000 B.t.u. loss per foot length per hour



b. 4,000 B.t.u. loss per foot length per hour

FIG. 10.—Tunnel kiln fired with natural gas. *Basis.*—1 hr.

as many mols of oxygen, or $(8.42)(2)(100/21) = 80.3$ mols of air. The per cent of excess air in this case is $(59.3/80.3)100 = 73.9\%$. With half the radiation loss, the fuel consumption is reduced nearly in proportion, actually to $(4.98/8.42)100$ or 59.1% of its value in the former case. However, 4.98 mols of gas require $4.98 \times 2 \times 100/21$, or 47.5 mols of air for combustion, showing that the per cent of excess air is increased to $(58.9/47.5)100 = 124\%$, *i.e.*, nearly doubled. Actually the absolute number of mols of excess air remains substantially constant (59.3 *versus* 58.9). This must be so, for in the preheating zone, of the total

heat required, 1,303,000 and 969,800 C.h.u., in the two cases respectively, 636,500 C.h.u. must be absorbed by the stock whatever the heat loss. This is from 48 to 65% of the total. This heat requirement necessitates the presence of a large amount of gas to throw the heat forward in the kiln and this in turn means the use of a large (absolute) number of mols of excess air. See Fig. 10 *a* and *b*.

Returning to the cooling zone, further information may be obtained from the figures. In the case of high radiation loss, only 57,500 C.h.u. were recovered from cooling the stock. Since there must be used a total of 80.3 + 59.3, or 139.6, mols of air in the combustion, if all the air used were passed through the cooling end before going to the burners, it would absorb only 57,500/139.6, or 412 C.h.u. per mol. As the heat content of air (N_2 or O_2) at 20°C. is 140 C.h.u., it would be heated to a temperature at which its heat content is 562 C.h.u. This temperature (Fig. 1) is about 80°C. When the radiation loss is now halved, the heat recovered is 297,500 C.h.u. and the mols of air used, 47.5 + 58.9 = 106.4. This gives a heat absorption of 297,500/106.4 = 2,790 C.h.u. per mol. Its final temperature would be that at which its heat content is 2,930, which is about 430°C.

The conviction that to secure furnace efficiency excess air should be suppressed to the lowest point compatible with good combustion is so widespread that it is worth while to analyze the factors which play a part in the furnace the very design of which demands a large air excess. The first factor is the necessity of uniformity of rate of heating of the stock, requiring, as mentioned above, what is called "throwing the heat forward in the kiln." The only thing which can carry heat to the stock before it reaches the combustion zone is hot gas, the heat available depending on the quantity and temperature of that gas. The initial temperature of the gas should be kept down, however, as otherwise at the hot end of the preheating zone the temperature differences between gas and stock will be excessive and the danger both of too rapid heating and of localized overheating correspondingly great. The difficulty due to such excessive and variable temperature differences can be met, as is sometimes done, by resort to indirect heating through flues, but where direct contact between combustion gases and the stock is allowable, it is cheaper and better to secure uniformity of heating by using

excess air. By this method it is easy to secure any desired ratio of the temperature differences at the two ends of the preheating zone and hence meet any required heating schedule, relatively fast at the start and slow at the end, or *vice versa*, or uniform throughout.

There are whole ranges of operation of such a kiln, however, in which excess air is essential to secure even thermal efficiency, entirely irrespective of heating schedule. With a wall loss of 8,000 B.t.u. per foot per hour, of the total heat supplied to this kiln in the fuel, 75% is lost through the walls. As already shown, this leaves almost no recoverable heat in the cooling zone. If, on the other hand, this loss be reduced by using more and better insulation, more recoverable heat is available, which must be picked up by the incoming air. Obviously, this air cannot be preheated above the temperature of the hot stock. If now the

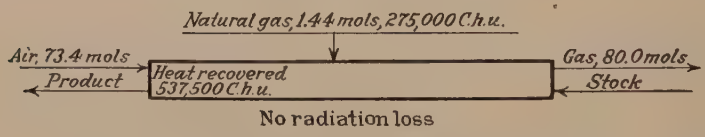


FIG. 11.—Tunnel kiln fired with natural gas with no radiation loss. (Hypothetical case). *Basis.*—1 hr.

wall loss be thus reduced to about 60% of the total heat input, theoretical air is insufficient to absorb this recoverable heat, and if a proper excess air be not used to absorb it, thermal efficiency will go down. Furthermore, the percentage excess required gets larger the more efficient the kiln. This applies to all furnaces preheating air by recovering sensible heat from the charge.

It is worth while to consider the hypothetical case of no radiation loss. The heat requirements for stock and car, of course, remain the same. If equations are set up similar to the above, solution shows 1.44 as the mols of gas required, and 59.7 mols of excess air. This is equivalent to 436% excess air. If this air absorbed all the heat given up by the stock in the cooling zone, it would be preheated to 1015°C. Hence, in this extreme case it is obvious that theoretical air could not possibly absorb the efficiently recoverable heat. See Fig. 11.

The second part of the design is the recalculation of the above figures so that flue requirements, etc. may be modified to take care

of the different gas volumes when a lower grade of fuel is used, namely, cold producer gas of the composition 7% CO_2, 21% CO, 15% H_2, 1% CH_4 and 56% N_2. The heat requirements of the stock and radiation losses are the same as before, so these need not be recalculated. For this gas the heat of combustion per mol is different from that of methane and so also is the theoretical air necessary for combustion.

Consider 1 mol of this gas. Using the lower heating values for the combustible gases present, its heating value is 0.21(68,000) + 0.15(58,000) + 0.01(191,000) = 24,900 C.h.u.

For a mol there is required to burn the CO, H_2 and CH_4, (0.21/2) + (0.15/2) + (0.01)(2) = 0.20 mol O_2. This brings in 0.20(79/21) = 0.752 mol N_2. Thus the products of combustion are shown in the subjoined table.

Original gas	Products of combustion		
	CO_2	N_2	H_2O
CO_2	0.07		
CO	0.21		
H_2	....	.....	0.15
CH_4	0.01	.....	0.02
N_2	....	0.56	
Air for combustion	....	0.752	
Total	0.29	1.312	0.17

In the combustion zone, on burning x mols of gas with y mols of excess air, the heat input (case I, 8,000 B.t.u. loss by radiation per hour per foot length) is 57,500 + 24,900x and the heat output to the stock 60,250 and for radiation, 66,700 C.h.u. The sensible heat in the gases is a different function of x and y from the former case. Using the difference in heat contents between 1330 and 20°C. and the mols of gas obtained, this becomes

$$(0.29x)(15{,}220) + (0.17x)(11{,}930) + (1.312x)9{,}860$$

for the theoretical products of combustion and 9,860y for the excess air. Upon addition and simplification these reduce to 19,500x + 9,860y.

Thus the heat balance for this zone is

$$57{,}500 + 24{,}900x = 19{,}500x + 9{,}860y + 60{,}250 + 66{,}700$$

for case I, and

$$297{,}500 + 24{,}900x' = 19{,}500x' + 9{,}860y' + 60{,}250 + 33{,}350$$

for case II (4,000 B.t.u. unit loss).

In the preheating zone, the heat input is

$$13{,}100(0.29x) + 10{,}020(0.17x) + 8{,}360(1.312x) + 8{,}360y = 16{,}480x + 8{,}360y.$$

This is obtained by multiplying the quantities of the different gases by the differences in their heat contents between 1330 and 240°C.

The output in this zone is the heat to the stock plus radiation loss. These are constants and will be the same for the combustion of any fuel. The heat balance for case I may be written as

$$16{,}480x + 8{,}360y = 636{,}500 + 666{,}700$$

and for case II

$$16{,}480x' + 8{,}360y' = 636{,}500 + 333{,}300.$$

Solution of the first pair of equations,

$$57{,}500 + 24{,}900x = 19{,}500x + 9{,}860y + 60{,}250 + 66{,}700 \text{ and}$$

$$16{,}480x + 8{,}360y = 636{,}500 + 666{,}700,$$

gives $x = 64.7$ and $y = 28.4$ and for the second pair,

$$297{,}500 + 24{,}900x' = 19{,}500x' + 9{,}860y' + 60{,}250 + 33{,}350 \text{ and}$$

$$16{,}480x' + 8{,}360y' = 636{,}500 + 333{,}300,$$

x' is 38.3, and y', 40.6.

The required air for 64.7 mols is $64.7(0.20)(100/21) = 61.6$ and 38.3 mols of producer gas need 35.5 mols of air. The first corresponds to 46% and the second to 114% excess air; 61.6 + 28.4 mols of air are preheated by 57,500 C.h.u. to 124°C. and 35.5 + 40.6 mols are heated to 575°C. by 297,500 C.h.u.

For completeness in comparison, it can similarly be shown that, when the radiation loss is reduced to zero, 11.0 mols of gas must be burnt, requiring 10.5 of air and using 54.5 in excess. This excess is 520% of the required.

The recoverable heat available in the stock would preheat even this air to approximately 1260°C. This temperature, being greater than that of the stock, cannot, of course, be reached,

but the heat can be recovered by preheating the producer gas by passing it through separate flues in the cooling zone. It is interesting to note that in this kiln natural gas has no advantage, thermal or otherwise, over producer gas. It would, of course, give more risk of localized overheating.

It is perhaps worth while to compute the heat consumption of an ideal kiln, *i.e.*, one in which there are no radiation or conduction losses and the stock and stack gases are completely cooled to the original temperature of stock and air. The total heat required to burn the stock has already been computed, namely,

	C.H.U.
Heat absorbed, 20 to 650°C	246,000
Heat of decomposition	77,500
Heat absorbed, 650 to 1110°C	186,500
Heat absorbed, 1110 to 1210°C	60,250
	570,250

In the ideal kiln, however, both burnt stock and water vapor formed by decomposition of the stock are cooled to 20°C., the former from 1210°C. yielding 438,000 C.h.u. and the latter 23,100 C.h.u. Subtracting these two quantities from the above total leaves 109,150 C.h.u. as the minimum possible heat consumption of an ideal furnace. On this basis, the thermal efficiency of the kiln can be computed. In a kiln with no wall loss, the heat efficiency is nearly 40%, with a loss of 4,000 B.t.u. per foot per hour less than 12% and with a loss of 8,000 B.t.u. per foot per hour less than 7%.

The following table brings together for comparison the results in the various cases.

	Natural gas			Producer gas		
B.t.u. loss per foot per hour	8,000	4,000	0	8,000	4,000	0
Mols gas required	8.42	4.98	1.44	64.7	38.3	11.0
Mols theoretical air	80.3	47.5	13.7	61.6	35.5	10.5
Mols excess air	59.3	58.9	59.7	28.4	40.6	54.5
Total mols air	139.6	106.4	73.4	90.0	76.1	65.0
Per cent excess air	73.9	124	436	46.0	114	520
Total mols stack gas[1]	152.3	116.5	80.0	148.3	113.7	79.2
Heat recovered in cooling zone, C.h.u.	57,500	297,500	537,500	57,500	297,500	537,500
Temperature preheated air, °C.	80	430	1,015	124	575	1,260
Total heat supplied,[2] C.h.u.	1,608,000	951,000	275,000	1,611,000	955,000	274,000
Heat loss by radiation, C.h.u.	1,213,700	606,700	0	1,213,700	606,700	0
Per cent radiation loss	75.6	63.8	0	75.1	63.6	0
Thermal efficiency, per cent	6.8	11.5	39.7	6.8	11.4	39.9

[1] Including 5.2 mols of water vapor due to loss of combined water by the stock.

[2] 191,000x for natural gas and 24,900x for producer gas.

PROBLEM

The kiln discussed in this chapter is to be modified by adding a drying section, the purpose of which is to make it possible to charge the kiln with partially dried stock, dry this in the new section and then complete the burning in the rest of the kiln, which remains as described. The stock will enter the drying section at the present temperature of 20°C.; will be heated to 80°C., without appreciable evaporation of moisture; the moisture will then evaporate at a substantially constant temperature of 80°C.; and the stock will then go on into the present preheating zone of the kiln, entering this zone at 80°C. The moisture content of the stock as charged will be 12%. The temperature of the gas leaving the preheating zone will be 260°C., and the temperature difference between the stock and gas throughout this zone is to be constant, as in the original kiln. Assuming a wall loss per foot of length per hour of 4,000 B.t.u. for all sections except the new drying section, a negligible loss through the walls of this section because of the low temperatures there prevailing, and assuming the use of the present natural gas as fuel, estimate the mols of this gas required per hour to handle the same weight of material on the dry basis as before.

CHAPTER VII

METALLURGY

In metallurgy, the roasting of sulfide ores is one of the important problems which may be solved by stoichiometric methods. However, the roasting of FeS_2 has already been covered in the chapter on Sulfur (p. 63), and it seems unnecessary to discuss the differences, stoichiometrically minor, between the roasting of the sulfides of the various metals. This chapter will be restricted to the reduction and refining operations in the metallurgy of iron. The applicability of the methods of computation to similar reactions in the treatment of other metals should be obvious.

Illustration 1.—The following figures are abstracted from the data sheet of a test on a blast furnace using hematite ore:

BLAST FURNACE

Data.—Reduced to 24-hr. basis.

Burden:	
Ore	2,150,000 lb.
Coke	1,048,500 lb.
Scale	151,800 lb.
Stone	414,000 lb.
Flue dust (dry basis)	120,000 lb.
Pig	1,203,600 lb.
Barometer	29.84 in.
Air temperature	72°F.
Relative humidity	82%
Average blast pressure	14.1 lb. per sq. in.
Average blast temperature	960°F.
Average top-gas temperature	330°F.

Analyses

	Per Cent		Per Cent
Ore:		Scale:	
Fe	51.6	Fe	72.68
Mn	0.83	Mn	0.57
S	0.032	Pig:	
H_2O	10.6	Fe	92.12
SiO_2	8.78	Si	1.36
Coke:		Mn	1.49
Fixed carbon	80.7	S	0.027
Vol. comb. matter	2.2	C	4.65
Moisture	4.4	Flue dust:	
Ash	12.7	Fe	41.4
B.t.u.	12,130	C	7.9
Total C (combined)	82.14	Gas:	
Total H (combined)	0.83	CO_2	14.1
Limestone:		CO	24.6
CaO	54.55	O_2	0.1
SiO_2	0.80	H_2	2.2
Moisture	0.70	N_2	59.0
Ignition loss	43.30		

Solution.—From the data it is immediately possible to set up an iron balance and a carbon balance. The first is a complete balance and gives a check on the accuracy of the data. The second gives the carbon in the gas by difference. The elements which tie together the gas analysis with the analyses of the components in the charge and product are carbon and oxygen. Therefore, the next step is to recompute the analyses of coke, pig and gas in terms of these two elements. The amount of gas leaving the furnace may now be computed by two independent means, *i.e.*, by a carbon balance and by an oxygen balance. This is the method of solution followed below.

Iron Balance

	Pounds
Input:	
Ore, 2,150,000(0.516) =	1,109,000
Scale, 151,800(0.7268) =	110,000
Total	1,219,000
Output:	
Pig, 1,203,600(0.9212) =	1,109,000
Dust, 120,000(0.414) =	50,000
Deficiency	60,000
Total	1,219,000

The table shows that the output of iron is about 5% less than the input. This may be due partly to iron in the slag, largely as emulsified nodules of pig. There is also the likelihood that the pig withdrawn from the furnace did not quantitatively correspond to the charge fed at the top. On a blast furnace it is necessary to have a long test period in order to make this error negligible.

CARBON BALANCE

	POUNDS
Input:	
Coke, 1,048,500(0.8214) =	861,000
Stone, 414,000(0.4330)(12/44) =	49,000
Total	910,000
Output:	
Pig, 1,203,600(0.0465) =	56,000
Dust, 120,000(0.079) =	9,500
Gas, by difference	844,500
Total	910,000
Ratio of C in stone to C in gas, 49,000/844,500 =	0.0580

Basis.—100 lb. coke.

Mols total H_2 = 0.83/2.016 =	0.411
Mols H_2O = 4.4/18 =	0.244
Mols net H_2 =	0.167
Atoms C = 82.14/12 =	6.85
Net H_2/C from coke = 0.167/6.85 =	0.0244

It is now necessary to compute the oxygen removed from the ore. The ratio of O:Fe in the hematite is 3:2. In the scale this ratio must be computed. The analysis shows that the scale contains 72.68% Fe and 0.57% Mn. No serious error will be introduced by calling the difference, 26.75%, oxygen. The composition of 100 lb. of scale is, therefore, as follows:

	POUNDS	ATOMS
Fe	72.68	= 1.301
Mn	0.57	= 0.010
O	26.75	= 1.671

Assuming manganese present as MnO, the ratio of O:Fe = 1.661/1.301 = 1.276. With this figure available, it is perhaps best to compute the oxygen equivalent of the pig.

Basis.—100 lb. pig (computation of equivalent oxygen).

Fe:	Atoms O
Ore, (92.12/55.84)(1,109,000/1,219,000) (3/2) =	2.251
Scale, (92.12/55.84)(110,000/1,219,000) (1.276) =	0.190
Mn,[1] (1.49/54.93)2 =	0.054
Si, (1.36/28.1)2 =	0.097
S, (0.027/32.07)3 =	0.003
Total O removed by reduction	2.595
Total O removed by reduction per 24 hr., 0.02595(1,203,600) =	31,200

Basis.—100 mols dry gas.

Gas	Mols	Atoms C	Atoms O	Mols H_2
CO_2	14.1	14.1	28.2	
CO	24.6	24.6	24.6	
O_2	0.1	....	0.2	
H_2	2.2	....	....	2.2
N_2	59.0			
Total	100.0	38.7	53.0	2.2
$O \div N_2 = 59(42/79)$			31.35	
C from stone, (49,000/844,500)38.7 =		2.25		
O from stone, 2(2.25)			4.50	
Net H_2 from coke, 38.7(861,000/844,500)0.0244			....	0.97
H_2 from decomposition of H_2O, by difference			....	1.23
O from decomposition of H_2O			1.23	
Total O accounted for			37.08	
O from ore, by difference			15.92	
			53.0	

Mols dry tunnel-head gas per 24 hr.

By carbon balance:

$$\frac{\text{Atoms C}}{12} \left| \frac{844{,}500}{38.7} \right| 100 = 181{,}700 \text{ mols}$$

By oxygen balance:

$$\frac{\text{Atoms O}}{15.92} \left| \frac{31{,}200}{} \right| 100 = 196{,}000 \text{ mols}$$

[1] This assumes all Mn as MnO_2. Were the amount large enough to justify it, the different forms present could be allowed for, as was done with iron.

While these two balances are based on analyses of the same materials, they are none the less independent except for the fact that in the oxygen balance the oxygen from the stone had to be computed from carbon data. The difference between the two values, about 8%, is a reasonable measure of the dependability of the data. The carbon balance, however, ought to be given more weight than the other, because on the gas basis oxygen from the ore represents a difference between relatively large quantities. Unless expensive equipment is available to measure the huge volume of gas leaving the furnace, balances of this sort

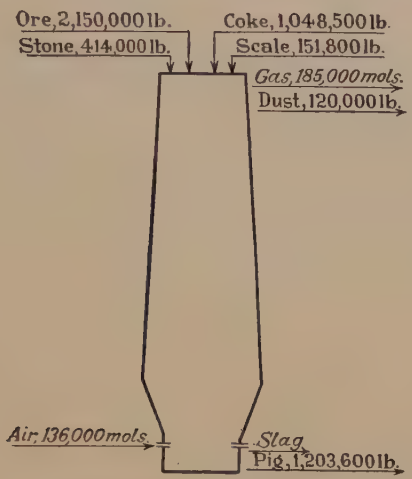


FIG. 12.—Blast-furnace problem. *Basis.*—24 hrs.

represent by far the easiest and most accurate method of determining its amount. See Fig. 12 for a diagrammatic representation of this problem.

It is instructive to compute the following quantities:

1. Volume of tunnel-head gas leaving the furnace per minute.
2. Volume of free air per minute at the blower intake, neglecting any possible leakage between the blower and the furnace.
3. B.t.u. as potential heat of combustion in the furnace gas, expressed as per cent of the heat of combustion of the fuel.
4. Percentage of the carbon in the coke charged which is burnt at the tuyères.

1. *Volume of tunnel-head gas.* First compute the amount of water vapor in the air and that formed on combustion.

Mols of water vapor:

a. From air, 72°F., 82% relative humidity; pressure H_2O = 0.82(0.79) = 0.65 in. Partial pressure of dry air = 29.84 − 0.65 = 29.19 in.

Mols dry gas	Mols N_2	Mols dry air		
181,700	59.0	100	0.65	
	100.0	79	29.19	= 3,020 mols H_2O

b. From coke:

1,048,500 (0.411/100)[1] = ...	4,310 mols H_2O
	7,330 mols H_2O
Mols leaving as H_2, 181,700(0.022) = ...	4,000
Mols left as H_2O = ...	3,330
Mols dry gas	181,700
Mols total gas	185,000

Mols gas per min.	Cubic feet S. C.	At 330°F.		
185,000	359	790	29.92	
(24)(60)		492	29.84	= 74,300 cu. ft. per minute

2. *Volume of free air per minute at the blower intake.*

Mols dry gas	Mols N_2	Mols air	Cubic feet dry, S. C.	Dry at 72°F., 1 atm.		
181,700	59.0	100	359	532	29.92	
(24)(60)	100.0	79		492	29.19	= 37,450 cu. ft. per minute

3. *B.t.u. as potential heat of combustion in the furnace gas.*
Basis.—1 mol dry tunnel-head gas.

Gas	Mols	Molal heat of combustion	Product
CO	0.246	68,000	16,700
H_2	0.022	68,300	1,500
			18,200

(181,700)(18,200)(1.8) = 5,950,000,000 B.t.u. potential heat.
Heat input: (1,048,500)(12,130) = 12,720,000,000 B.t.u.

[1] This is really the water equivalent of the hydrogen in the coke.

Potential heat of combustion as per cent of the heat input:

$$(5{,}950{,}000{,}000/12{,}720{,}000{,}000)100 = 46.7\%.$$

Of every 100 heat units charged to the furnace as heat of combustion of the coke fuel, 46.7 units leave the furnace as potential heat of combustion in the gas. It must, however, be remembered that heat also enters the furnace as sensible heat in the blast.

4. *Percentage of the carbon in the coke charged which is burnt at the tuyères.* At the very high temperature of the bottom of the blast furnace, CO_2, which is the primary product of combustion of carbon in air, is reduced with extreme rapidity by contact with more carbon, substantially completely to CO. This must be the condition in the bottom of the furnace, since CO_2, if present in quantity, would reoxidize the iron to the oxide. It therefore follows that in the tuyère zone there must be consumed an amount of carbon substantially equivalent to quantitative conversion of the oxygen in air to CO. There is actually consumed an additional amount corresponding to the conversion of some of the nitrogen to cyanogen, but this will be neglected.

Mols dry gas	Mols N_2	Atoms O = atoms C	Pounds coke		
181,700	59.0	42.0	100	100	
	100.0	79.0	6.85	1,048,500	= 79.5%

Illustration 2.—A blast furnace producing ferromanganese from a pyrolusite ore yields a product containing 77.1% Mn, 15.9% Fe and 5.7% C. The dolomitic limestone consumption averages 2,500 lb. per long ton of ferromanganese produced. This stone contains 43.7% CO_2. It is impossible to reduce all the manganese out of the slag and on the basis of plant experience it is found that the manganese left in the slag averages 20% of that in the product. The coke employed contains 87% C and 0.4% H, on a dry basis. The gas is 7.1% CO_2, 30.3% CO, 3.2% H_2 and 59.4% N_2. Compute the coke consumption per long ton of ferromanganese produced.

Solution.—From the gas analysis it is possible to compute the oxygen in the gas other than that coming from the air. This excess oxygen must come from the ore, the CO_2 from the limestone and any reduction of water vapor to hydrogen which may take place in the furnace. Similarly, from the analysis of the ferromanganese one can determine the equivalent amount of oxygen given up in the furnace. Furthermore, since the quanti-

ties of manganese in the slag and of limestone used for flux are given in terms of the product, this oxygen equivalent of the ferromanganese can be corrected for the oxygen corresponding to partial reduction of that part of the manganese which goes into the slag and for the CO_2 from the limestone. Therefore, the first thing to do is to recompute the analytical data in this way, simultaneously expressing the analysis of the coke on a molal basis.

Basis.—100 mols dry gas.

	Mols	Atoms C	Atoms O
CO_2	7.1	7.1	14.2
CO	30.3	30.3	30.3
H_2	3.2		
N_2	59.4		
Total	100.0	37.4	44.5
O $\simeq$ N_2 = 59.4(42/79) =			31.58
O $\simeq$ ore + stone + H_2O reduced (by difference) =			12.92

Basis.—100 lb. coke.

	Pounds	
C	87.0	7.25 atoms C
H_2	0.4	0.198 mol H_2

Basis.—100 lb. ferromanganese.

	Pounds	Atoms	Atoms of O equivalent
Mn	77.1	1.405	2.810
Fe	15.9	0.285	0.428
C	5.7	0.475	
Si (difference)	1.3	0.046	0.092
Total	100.0	.....	3.330
O $\simeq$ Mn in slag, 0.2(1.405) =			0.281
C in stone, (2,500/22.4)(0.437/44) = 1.108 atoms			
O $\simeq$ C in stone =			2.216
Total O in gas from ore and stone =			5.827

Now let x = pounds coke consumed per 100 lb. ferromanganese. $\therefore$ C in gas = that in coke plus that in stone minus that in product = $0.0725x + 1.108 - 0.475 = 0.633 + 0.0725x$. Likewise, the hydrogen in the gas from the coke = $0.00198x$.

There are now exact expressions for the total carbon in the gas on two separate bases, *i.e.*, per 100 mols of dry gas and per 100 lb. of ferromanganese. Similarly, on the two same bases there are expressions for oxygen by difference. However, on the ferromanganese basis this figure, 5.827 atoms, is for oxygen from ore and stone alone, whereas on the gas basis the figure, 12.92 atoms, is oxygen from ore, stone and water reduction. Therefore, it is not certain that these two figures are comparable.

First, tentatively assume that the hydrogen in the gas comes solely from the net hydrogen in the coke and corresponds quantitatively thereto, there being no water reduction. If this be true, the oxygen by difference, 12.92 atoms, must come from ore and stone alone. Therefore the ratio of total carbon in the gas to total oxygen given up by ore and stone may be expressed, first, on a ferromanganese basis and, second, on a gas basis. By equating the two, the following expression is obtained:

$$\frac{0.633 + 0.0725x}{5.827} = \frac{37.4}{12.92};$$ whence x = 224 lb. of coke per 100 lb. of product.

It is improbable, however, that no water reduction took place in the furnace. Suppose for the moment that the coke had contained no hydrogen whatever. In that case all the hydrogen in the gas must have come from water reduction. Since the hydrogen is 3.2 mols, it follows that the oxygen going into the gas from reduction of water vapor would be 3.2 atoms, leaving 9.72 atoms from ore and stone. Therefore, again, the two expressions for the ratio of carbon to oxygen from ore and stone may be equated, *i.e.*,

$$\frac{0.633 + 0.0725x}{5.827} = \frac{37.4}{9.72};$$ whence x = 301 lb. of coke per 100 lb. of product.

Both these assumptions are wrong. Part of the hydrogen comes from the coke and the rest from water reduction. Therefore, on the gas basis, the oxygen from ore and stone is less than 12.92 but more than 9.72 atoms. Consequently, the coke figured on the first assumption is too low a value and on the second too high. On the other hand, inspection of the two equa-

tions set up shows that the left-hand side is the same in both cases and truly represents the ratio of total carbon in the gas to total oxygen given up to the gas from ore and stone. Furthermore, the numerator on the right-hand side of the equation, 37.4 atoms of C, is exact. It only remains to correct the denominator of this fraction. Now, on the ferromanganese basis one has an exact expression for both total hydrogen from the coke and total carbon in the gas. The ratio of these makes it possible to earmark that part of the hydrogen in the gas which comes from the coke. Subtracting this hydrogen from the total hydrogen in the gas gives the hydrogen formed by water reduction. This yields the equation,

$$\frac{0.633 + 0.0725x}{5.827} = \frac{37.4}{12.92 - \left(3.2 - 37.4\frac{0.00198x}{0.633 + 0.0725x}\right)};$$

whence $x = 272$ lb. of coke per 100 lb. of product, the correct value for the coke consumption. This corresponds to 22.4 times this amount, or 6,090 lb. of coke per long ton of ferromanganese.

This result is obtained by a comparison of the analyses of gas and product and, in so far as the data are dependable, the result is correct. This does not mean, however, that 6,090 lb. of coke were charged to the furnace per ton of ferromanganese drawn into the molds. For example, any product lost by emulsification in the slag, while not available to the plant, is none the less included in the 100 lb. of ferromanganese used as a basis in this problem. Similarly, the coke consumption figured is coke actually reacting in the furnace and would not include any coke dust blown out the top with the gas. It is necessary to keep such corrections clearly in mind when comparing a computed result with plant figures.

Because the solution of this problem depends on the ratio of carbon to oxygen in ore and stone, and, in the case of the gas, this oxygen is obtained as a difference between relatively large quantities, the result is very sensitive to slight errors in the gas analysis, whether due to poor sampling or carelessness in the analysis itself. Thus, if the CO_2 in the gas analysis as given above is assumed too low, and the CO too high, by 0.5% each, the coke consumption computed by the above method becomes 6,200 lb. per ton of product, an error of 4.6%. Since the analysis of so simple a gaseous mixture should be accurate to at least a

quarter of 1%, the coke consumption computed in this way should be accurate roughly to 2 to 4%. Furthermore, it is obvious that the whole method depends on an accurate knowledge of the state of oxidation of the components of the ore.

If the production rate of the furnace is known, it is then possible to compute the rate of air consumption, the gas production and similar values, as was done in the preceding problem.

Illustration 3.—An open-hearth furnace is fired with a producer gas of the following analysis: 3.9% CO_2, 0.3% illuminants (C_3H_6), 26.7% CO, 4.3% CH_4, 10.4% H_2 and 54.4% N_2. The coal used in the producer contains 78.8% C. At 4:40 a.m., the whole charge having been previously melted and brought up to 2820°F., ore is added. Forty minutes later a sample of the stack gas at the outlet of the checkers is taken and found to contain 14.0% CO, 6.8% O_2 and 79.2% N_2. At this time in the heat, the producers are being run at a coal consumption rate of 4,350 lb. per hour. The steel production of this furnace is 250,000 lb. per heat. Calculate the rate at which the carbon content of the steel is being reduced, expressed as per cent per hour at the time the stack-gas sample was taken, *i.e.*, at 5:20 a.m.

Solution.—The carbon is eliminated by interaction of the carbon in the molten steel with the iron oxide in the slag. At this temperature this reaction produces almost pure CO. The gas must, however, bubble out through slag containing FeO, the only oxide of iron likely to be present this long after the addition of ore. FeO will oxidize the CO to CO_2, but at this temperature the equilibrium of the reaction is only a little under 90% CO. Since the oxidation will not reach equilibrium, no appreciable error will be made by assuming that the gas leaves the bath 90% CO and 10% CO_2.

Basis.—100 mols flue gas.

Gas	Mols	Atoms C	Mols O_2
CO_2	14.0	14.0	14.0
O_2	6.8	....	6.8
N_2	79.2		
Total	100.0	14.0	20.8

Basis.—100 mols of producer gas.

Gas	Mols	Atoms C	Mols O_2	Mols H_2
CO_2	3.9	3.9	3.9	
Ill. (C_3H_6)	0.3	0.9	.....	0.9
CO	26.7	26.7	13.35	
CH_4	4.3	4.3	.....	8.6
H_2	10.4	....	.....	10.4
N_2	54.4			
Total	100.0	35.8	17.25	19.9

O_2 required for combustion, $35.8 + 19.9/2 - 17.25 = 28.5$
N_2 ≈ O_2 required for combustion, $28.5(79/21) = 107.2$
Let x = mols excess air used in combustion
y = atoms C brought in from bath.
Total C in flue gas = $35.8 + y$
Total O_2 in flue gas = $35.8 + 0.90y/2 + 0.10y + 0.21x$
Total N_2 in flue gas = $54.4 + 107.2 + 0.79x$

$$\frac{C}{N_2} \text{ (in flue gas)} = \frac{35.8 + y}{54.4 + 107.2 + 0.79x} = \frac{14.0}{79.2}$$

$$\frac{O_2}{N_2} \text{ (in flue gas)} = \frac{35.8 + 0.55y + 0.21x}{54.4 + 107.2 + 0.79x} = \frac{20.8}{79.2}$$

Solving these equations simultaneously,

$$x = 134;\ y = 11.5.$$

This means that for every 35.8 atoms of C from the fuel, *i.e.*, from the producer gas or ultimately from the coal, 11.5 atoms of C are evolved from the steel.

Hence the rate of carbon removal from the bath is

$$\frac{\text{Pounds C per hour}}{4{,}350(0.788)} \times \frac{\text{C per hour from the steel}}{11.5} \times \frac{100}{250{,}000} = 0.44\% \text{ reduction per hour in the carbon content of the steel}^1$$

The actual rate of reduction, as determined by direct analysis, of the metal was 0.47%.

[1] The weight of metal should be corrected for carbon and other elements removed, iron formed by reduction, etc., but the error is small.

The result computed in this way depends for its accuracy not only on proper sampling of the flue gas (easily done at the checker outlet) but also on an exact knowledge of the firing rate at the time the flue-gas sample is taken. If the producers are fired at uniform rate, the computation may be based on the ultimate analysis of the coal instead of on that of the producer gas (see Chap. III).

CHAPTER VIII

STOICHIOMETRY OF PLANT DESIGN

There are two ultimate functions of industrial stoichiometry. The first of these is to permit analysis of data representative of present plant operations, the calculation of quantities otherwise difficult of direct measurement and, in general, the securing of an accurate and quantitative vision of what is actually taking place within a process, thus providing information which, without the aid of this tool, would be entirely wanting or at best only empirical and qualitative in nature. Hitherto, discussion has been devoted almost exclusively to illustrations of this important function.

The second and no less important purpose is the interpretation of laboratory data in terms of large-scale production. One type of problem falling under this second head is the design of equipment for a process, having available as data the physical and chemical characteristics of the materials involved, and another is the design of large-scale units from data obtained by laboratory experimentation upon a process in the development stage.

As an example of the first type, the tunnel kiln is widely used for burning brick and other ceramic ware. The design of such a kiln for the manufacture of a particular kind of brick for which, perhaps, it has not hitherto been employed, reduces itself to a question not of fundamental laboratory research, but of finding the heat requirements of the materials, of deciding upon the fuel to be used, of estimating radiation losses, etc. Given these estimates and certain characteristics of the materials involved in the construction, one may proceed with the actual design of the kiln itself. The methods by which the stoichiometric problems involved in such design are solved are illustrated in Chap. VI on the Stoichiometry of Furnace and Kiln Design.

It is the purpose of this chapter to indicate the methods by which the other type of problem may be treated, *viz.*, the calculation from data obtained on a small scale in the laboratory, of plant and equipment for full-scale operation and the estimation of the performance to be anticipated from such equipment.

In the development of any new proposition, whether it be based upon a newly discovered reaction, the utilization of an old reaction for a new purpose or the introduction of a process used elsewhere, data for which are not available, the inexperienced worker is prone to do his first experimentation upon entirely too large a scale. Such development should always be stepwise. The first stage is the thorough study of the proposition by the ordinary methods of the laboratory. The second stage should involve carrying out the process on the largest laboratory scale compatible with reasonable precision and dispatch, but duplicating, so far as practicable, the concentrations, pressures, temperatures, times of reaction and other operating conditions which, so far as can be foreseen, will obtain in plant operation. The next step is the construction of a single full-scale unit. This is followed by development on a semicommercial scale which, if the process be successful, will grow into the full commercial plant. At the end of each of these stages of development, it is imperative to subject the results obtained to critical analysis, in order to base thereon an intelligent decision as to the advisability of further development and, in case such development is justifiable, to design equipment for the next stage on the basis of the data already obtained.

At the end of any one stage of development, however early in the series this may be, in order to form an intelligent opinion as to the ultimate practicability of the process, it is usually necessary to make tentative designs and estimates of the ultimate plant, even though the next stage in development may be on a much smaller scale. Otherwise, estimates as to commercial practicability may be very misleading. It is obvious that the methods of computation will be substantially parallel, whatever the proposed increase in scale of operation may be. The following illustrations will, therefore, be limited to the estimation of the ultimate plant from data obtained on large-scale laboratory experimentation. This does not imply that, in the process of development, the full-scale plant is the next thing to construct.

While the methods employed in such computations are broad in character and applicability, it is difficult to appreciate them fully when they are presented in general terms, and hence it is deemed best to develop them in connection with the solution of specific problems.

Illustration 1.—It is proposed to manufacture iron-oxide red by the following process: Commercial ferrous sulfate is dissolved in water and precipitated with a solution of sodium carbonate.

The sludge thus obtained is very gelatinous, difficult to filter and practically impossible to wash free of sodium sulfate. It can, however, be drained on a filter to a reasonable consistency and, if then dried and heated to not less than 150°C., it is dehydrated and its colloidal character so completely destroyed that it can readily be washed. The washed precipitate must now be ignited in a stream of air to a temperature not less than 705 and not more than 725°C. If the temperature is too low, the red color of the product is not fully developed, but the oxide is of a yellowish hue. If heated too hot, the color becomes purplish and the product loses its covering power.

In order to secure data upon which to base the design of equipment for the process and a decision as to its commercial practicability, the following experiment was conducted: 1,340 g. of soda ash containing 56.5% Na_2O were dissolved in water to give a solution weighing 3,680 g. and having a specific gravity of 1.27. This was filtered from insoluble matter on a cloth filter. The solution covered 50 sq. in. of filter area and passed through in $1\frac{1}{2}$ min. under a head averaging 1 in. of solution. A second solution weighing 5,400 g. (specific gravity, 1.38) was made by dissolving in water 3,000 g. of copperas containing 22.5% Fe. Upon mixing the two solutions at a reasonably uniform rate, frothing took place to the extent of 30% of the combined volume. The total time required for mixing was 40 min.

Filtration of the resultant sludge on 200 sq. in. of cloth filter under a filtering head of $2\frac{1}{2}$ in. was accomplished at an average rate of 650 cc. per hour. The wet sludge thus obtained weighed 2,700 g. and had a specific gravity of 1.6. After drying under heat, the weight was reduced to 1,260 g. and the specific gravity to 1.1. The sludge then being in condition to wash, 3,000 cc. of wash water were used on 80 sq. in. of filter under a head of $2\frac{1}{2}$ in., the time required to pass through being $5\frac{1}{4}$ hr. The precipitate was then heated to 715°C. for 40 min., the temperature being controlled to within 10° of this point. Before heating, the weight was 2,250 g. and after heating 987 g., the rouge so obtained containing 97.2% Fe_2O_3.

Basing calculations upon the above data, it is proposed to make a preliminary estimate of the quantities of materials and sizes of equipment required to produce 5 tons of oxide per day, and also to calculate the efficiency of the process as carried out on the laboratory scale.

There are many ways of making the required conversion from metric to English units and from small to large scale, but the following is one of the easiest to visualize. This laboratory experiment employed 1,340 g. of soda ash and 3,000 g. of copperas and produced 987 g. of product. The corresponding figures are shown in the left-hand column of the subjoined table. Imagine a new experiment performed, using this same raw material and going through the same process, but starting with 1,340 lb. of

Grams	Material	Pounds
1,340	Soda ash taken	1,340
3,680	Solution formed	3,680
3,000	Copperas taken	3,000
5,400	Solution formed	5,400
2,700	Wet sludge obtained	2,700
1,260	Dry sludge obtained	1,260
2,250	Sludge after washing	2,250
987	Final oxide	987

soda ash and 3,000 lb. of copperas. It is obvious that the product would be 987 lb. of oxide and that the data could be tabulated as in the right-hand column of the same table, the figures being identical with those in the left-hand column but here signifying pounds instead of grams. It should, however, be clear that this identity of numerical values applies only to weight figures in the two cases, *i.e.*, in the actual experiment and the hypothetical one. In the second table, the data of the first are rearranged and expanded. The first column of figures gives the laboratory data. The second column gives the equivalent data for the hypothetical case of using pounds instead of grams. In this table, however, volumetric data are also included. The specific gravity of a material, being merely the ratio of its weight to that of an equal volume of water, is, obviously, numerically the same in all systems of units. The density of a material, its weight per unit volume, is its specific gravity times the density of water. In metric units the density of water is nearly unity, its absolute value depending on the temperature. In this problem its deviation from unity is neglected. Similarly, the density of water in English units is taken as 62.4 lb. per cubic foot. Hence, English density is obtained by multiplying metric

	Laboratory data	Equivalent data in English units	Plant data (10,000 lb. product)
Weight soda ash taken	1,340 g.	1,340 lb.	13,580 lb.
Weight solution formed	3,680 g.	3,680 lb.	37,280 lb.
Density of this solution	1.27 g. per cc.	79.25 lb. per cubic foot	79.25 lb. per cubic foot
Volume of this solution	2,898 cc.	46.45 cu. ft.	470.5 cu. ft.
Weight copperas taken	3,000 g.	3,000 lb.	30,390 lb.
Weight solution formed	5,400 g.	5,400 lb.	54,720 lb.
Density of this solution	1.38 g. per cc.	86.1 lb. per cubic foot	86.1 lb. per cubic foot
Volume of this solution	3,913 cc.	62.75 cu. ft.	635.5 cu. ft.
Weight of wet sludge	2,700 g.	2,700 lb.	27,350 lb.
Density of wet sludge	1.6 g. per cc.	99.8 lb. per cubic foot	99.8 lb. per cubic foot
Volume of wet sludge	1,687 cc.	27.05 cu. ft.	274 cu. ft.
Weight of dry sludge	1,260 g.	1,260 lb.	12,770 lb.
Density of dry sludge	1.1 g. per cc.	68.65 lb. per cubic foot	68.65 lb. per cubic foot
Volume of dry sludge	1,145 cc.	18.35 cu. ft.	186 cu. ft.
Weight wash water	3,000 g.	3,000 lb.	30,300 lb.
Weight wet oxide	2,250 g.	2,250 lb.	22,800 lb.
Weight dry oxide (product)	987 g.	987 lb.	10,000 lb.

density by this figure. In any units, volume is obtained by dividing weight by density. Further explanation of the first two columns of figures is unnecessary.

The plant is, however, required to produce 10,000 lb. of oxide per day, *i.e.*, 10,000/987 = 10.13 times the output of the hypothetical scale of the second column. Hence, the scale of the plant, both in weight and volume, is 10.13 times as great. The third column of figures represents the plant scale required and the quantity figures in it are obtained by multiplying the corresponding ones of the second column by 10.13.

A little thought will make it clear that the middle column of figures can easily be discarded. Doing so is equivalent to making the conversion by the following sort of proportion: If 3,000 g. of copperas produce 987 g. of oxide, then x lb. of copperas will produce 10,000 lb. of oxide, *i.e.*,

$$3{,}000\text{g.}/987\text{g.} = x \text{ lb.}/10{,}000 \text{ lb.}, \text{ or } x = (10{,}000/987)3{,}000 = 10.13(3{,}000) = 30{,}390 \text{ lb.}$$

This method of working the problem by proportion is entirely legitimate, but it is necessary to make sure that the units cancel. It is thus seen that the ratio 10,000/987 = 10.13 is a sort of conversion factor for weights only, directly from grams on an experimental scale to pounds on a plant scale.

It is obvious that equipment must be provided of capacity ample to handle the volumes and quantities thus computed, including adequate allowance for factors such as frothing and the

like. The design of such equipment, other than this computation of its capacity, is beyond the scope of this book.

Illustration 2.—Assume that it be desired to produce a solution of NaOCl from one of $CaOCl_2$ by precipitation with soda ash. It is understood that the product is to be decanted from the precipitate and the precipitate washed three times by decantation, using equal volumes of wash water each time, totaling sufficient to make up the next batch. The reason for this is the impracticability of concentrating dilute bleach solutions. The following data were taken from a laboratory experiment:

Weight of bleaching powder taken	286 g.
Weight of water for solution	1,660 g.
Weight of solution	1,946 g.
Specific gravity of solution	1.085
Cubic centimeters of thiosulfate (0.1107*N*) for 2-cc. sample	30.07 cc.
Weight of soda ash	300 g.
Weight of water to dissolve	1,900 g.
Weight of solution	2,200 g.
Specific gravity of solution	1.118 g.
Cubic centimeters of HCl (0.1856*N*) for 2-cc. sample	26.42 cc.
Calculated soda ash solution required, assuming bleach = 45% CaO, using 10% excess	2,060 g.
Extra water added	45 g.
Total weight mixed solutions	4,050 g.
Depth original solution	8.0 in.
Settling time to 2 in.	2 hr.
Temperature	25°C.
Volume decanted	2,760 cc.
Volume sludge	924 cc.
Cubic centimeters thiosulfate for 2-cc. product	13.46 cc.
Specific gravity of product	1.066
Wash water No. 1:	
Specific gravity	1.030
Volume	1,330 cc.
Thiosulfate for 2 cc	6.03 cc.
Wash water No. 2:	
Specific gravity	1.020
Volume	1,340 cc.
Thiosulfate for 4cc	5.84 cc.
Wash water No. 3:	
Specific gravity	1.010
Volume	1,335 cc.
Thiosulfate for 6 cc	5.08 cc.
Sludge:	
Volume	910 cc.
Thiosulfate for 4 cc	4.01 cc.

In this problem, the complication arises from the fact that in the laboratory the solution was made up with water, whereas in the plant wash waters from a previous batch will be used. If such wash waters were available in the laboratory, plant conditions could be simulated. The experiment might be repeated in the laboratory, always maintaining the same concentration of available chlorine in the product in every experiment, until conditions paralleling plant operation are realized, but it is easier to compute this. If the experiment had been repeated in the laboratory, the second run would not have been comparable with balanced plant operation, because in the first run an amount of bleach had to be used sufficient not only to supply the product but also to make up the hypochlorite carried in process in the wash waters. Hence, the amount of sludge was unduly large and the product correspondingly small. In the second operation, the sludge would be unduly small and the product large. Finally, however, after a sufficient number of repetitions, say n operations, these variations will iron out. Hence, the problem is to compute the conditions that will obtain upon the nth operation.

Study of the data shows that the volumetric concentration of available chlorine in the sludge is somewhat higher than in the supernatant liquid, perhaps due to a slight adsorption on the sludge. Except for this, the proportion could be written:

$$\frac{\text{Available chlorine in sludge}}{\text{Total available chlorine in solution}} = \frac{\text{Volume of sludge}}{\text{Total volume of solution}},$$

the solution being the sum of sludge and supernatant liquid. It is probably allowable to correct for the excess chlorine in the sludge by using a factor α, assumed constant, such that,

$$\frac{\text{Available Cl in sludge}}{\text{Available Cl in solution}} = \alpha\frac{\text{Volume of sludge}}{\text{Volume of solution}}.$$

Assuming as a basis a definite, constant total volume of solution,[1] V, after precipitation but before decantation, use the following nomenclature:

A = total weight of available chlorine in process.
B = weight of available chlorine in product.
C = weight of available chlorine in combined wash waters.
D = weight of available chlorine left in sludge.
v = volume of sludge.

[1] This includes the volume of the precipitate.

Designate laboratory (*i.e.*, first operation) conditions by the subscript 1; the absence of a subscript indicates final or nth operation conditions, still, however, assumed to be carried out on a laboratory scale and always under conditions chosen to produce the same concentration of available chlorine in the decanted product.

After decantation of the product in the laboratory, the chlorine left behind was $C_1 + D_1$. Since the volume of water required to make up a batch is V, the volume available for each wash is $V/3$. From the proportions given above, it follows that the chlorine left behind in the sludge after the first wash is

$$(C_1 + D_1)\left(\frac{\alpha v_1}{v_1 + V/3}\right);$$ after the second,

$$(C_1 + D_1)\left(\frac{\alpha v_1}{v_1 + V/3}\right)^2;$$ and after the third,

$$(C_1 + D_1)\left(\frac{\alpha v_1}{v_1 + V/3}\right)^3,$$ which must equal D_1.

Using this expression, α can be computed from the laboratory data, getting $\alpha = 1.2$.

The laboratory data show a loss of about 1.5%. Probably this is largely due to chemical decomposition. A constant chemical loss of this amount will be assumed under all conditions.

For nth operation conditions the following equations can be written:

$$B + C + D + 0.015A = A \tag{1}$$

$$\frac{C + D}{0.985A} = \frac{\alpha v}{V} \tag{2}$$

$$D = (C + D)\left(\frac{\alpha v}{v + V/3}\right)^3 \tag{3}$$

$$v/v_1 = (A - C)/A \tag{4}$$

The first of these is an available chlorine balance on the operation. The second is the distribution proportion discussed above, applied to the first decantation of product from sludge. The third is the same proportion applied to the washes. The fourth equates the ratio of the sludge in the nth operation to that in the first to the ratio of the bleach added in the nth to that used in the first. The volume of sludge is certainly proportional to the lime added, granting constant conditions of precipitation and decantation. Algebraic transformation of these equations gives

$$\frac{v}{v_1} = 1 - 0.985\frac{\alpha v}{V}\left[1 - \left(\frac{v}{v + V/3}\right)^3\right].$$

Since $V = 4{,}005$, $\alpha = 1.2$ and $v_1 = 910$, it is possible to solve this equation for v by successive approximation. This gives $v = 729$. In other words, if this laboratory experiment had been continued repeatedly until nth operation conditions were realized, the sludge would have been only 729 instead of 910 cc. and the product decreased to the difference between the total volume, 4,005 cc., and this, or 3,276 cc.[1] The nth operation product, corresponding to this larger volume, is $B = 86.55$ g. Hence, from the distribution proportion between sludge and total liquid, Eq. (2), $C + D = 24.2$ and from Eq. (3), $D = 1.84$ g., as compared with a sludge loss of 3.58 g. in the first run. Similarly, $A = 112.4$. The chemical loss in each operation is assumed to be 1.5% of 112.4 = 1.7 g., and therefore the total loss is this plus 1.84 g., or 3.54 g. Hence, the chlorine required in each operation is the product plus this, or 90.1 g., and the total percentage loss is 3.9%. The most essential data relative to nth operation on a laboratory scale may, therefore, be tabulated as follows:

Total chlorine in process	112.4 g.
Total volume of main solution	4,005 cc.
Volume of product	3,276 cc.
Volume of sludge	729 cc.
Chlorine in product	86.55 g.
Chlorine returned from previous run	22.36 g.
Chlorine loss	3.5 g.
Per cent of chlorine in product	2.82

Were it required to carry out this process, using in each case the wash waters from the previous batch, operating to produce a 2.82% product containing 1,000 lb. of available chlorine from each batch, the conversion of this table to English units can be made by the methods of the preceding problem, first assuming that the experiment had been carried out in pounds instead of grams and then increasing the scale in the ratio of 1,000/86.55. All weights are converted by this factor alone. The volume of the product may be found by getting its weight on a laboratory scale by multiplying its volume by its density, 4,005(1.066) = 4,270 g., converting this to pounds on a plant scale by multiply-

[1] Note that in the laboratory experiment too much wash water was used, so that the total chlorine in process in the laboratory cannot be used at this point. The computations assume nth operation expanded to a total volume of 4,005 cc.

ing by the factor, 1,000/86.55 and then reducing this to cubic feet by dividing by English density, (1.066)(62.4), obtaining thus a total volume of 742 cu. ft. It will be noted, however, that in doing this the specific gravities cancel. Thus consider the sludge, the gravity of which is unknown. Call this gravity s. Hence, the laboratory weight of sludge was $729s$ and the plant weight is $729s(1{,}000/86.55)$ lb. Hence, the plant volume is this divided by English density, $62.4s$, or

$$729(1{,}000/86.55)/62.4 = 135 \text{ cu. ft.}$$

The factor converting weights from one scale to the other converts any volume on the first scale to the volume of an equal weight of water on the second.

Basis.—1,000 lb. available chlorine produced each batch.

Total chlorine in process	1,299 lb.
Total volume of main solution	742 cu. ft.
Volume of product	607 cu. ft.
Volume of sludge	135 cu. ft.
Chlorine in product	1,000 lb.
Chlorine returned from previous run	258 lb.
Chlorine loss	41 lb.
Per cent of chlorine in product	2.82

In the laboratory experiment, the input was 105.9 g. of available chlorine. However, there were recovered in the wash waters 27.9 g., leaving, after crediting this, a net input of 78.0 g. The product was 72.9 g. and the loss, therefore, 5.1 g. Of this 3.6 g. were accounted for in the sludge due to incomplete washing and the rest, 1.5 g., were caused by decomposition and other losses. The percentage loss was, therefore, $100(5.1/78.0) = 6.54\%$, and the percentage chlorine efficiency 100 minus this, or 93.46%. On the other hand, it was shown above that under nth operation conditions the total percentage loss is 3.9%, only 60% as great as the laboratory loss. The corresponding chemical efficiency of the nth operation is 96.1%. This higher efficiency is due to the fact that, when part of the chlorine in process is returned in the wash waters from the previous batch, the volume of sludge is lessened, since the wash waters contain no calcium to be precipitated. Since the amount of wash water available is fixed, the smaller sludge is washed more completely and the losses thereby reduced. It is essential to keep in mind the fact that, whenever material is recovered from a process for recycling, the efficiency realized in the laboratory does not represent that

to be anticipated in the plant, but must be corrected for this recycling effect. It will be shown in the next problem that recycling does not always result in an increase in efficiency over that of the laboratory.

Illustration 3.—The following is the data sheet of a laboratory experiment on the production of sal soda by recrystallization of soda ash, with particular reference to the elimination of chloride from the product.

Weight of soda ash	5.0 lb.
Bulk density of soda ash	0.673 g. per cc.
Angle of slip	43 deg.
Weight of water	12.5 lb.
Time of solution	34 min.
Temperature of solution	77°C.
Weight of solution	17.2 lb.
Specific gravity of solution	1.280
Soda ash analysis:	
Na_2O	57.1%
CO_2	42.1%
Cl	0.40%
Time of filtration	32 min.
Area of filter	126 sq. in.
Depth of filter	2.85 in.
Weight of filtrate	16.6 lb.
Temperature of filtrate	51.3°C.
Specific gravity of filtrate	1.289
Weight of wash water	5.59 lb.
Temperature of wash water	40.9°C.
Specific gravity of wash water	1.009
Analysis of wash water:	
Na_2O	0.66
CO_2	0.49
Cl	0.009
Time of crystallization	25 hr.
Weight of batch	16.1 lb.
Temperature of batch	23°C.
Weight of mother liquor	5.91 lb.
Temperature of mother liquor	22°C.
Specific gravity of mother liquor	1.203
Analysis of mother liquor:	
Na_2O	10.83%
CO_2	7.50%
Cl	0.29%
Weight of wash water No. 2 (from washing crystals)	3.39 lb.
Temperature of wash water	20°C.
Specific gravity of wash water	1.104

Analysis of wash water:	
Na_2O	7.56%
CO_2	5.24%
Cl	0.155%
Weight of product	10.0 lb.
Bulk density	0.901 g. per cc.
Angle of slip	46.1 deg.
Analysis of product:	
Na_2O	20.89%
CO_2	14.93%
Cl	0.009%

Under plant conditions, it is obvious that the soda ash would be recrystallized from a solution made up partly with the wash waters and mother liquor from the previous batch and partly with fresh soda ash. The chloride would accumulate in the mother liquor. Assuming that each time a recrystallization is carried out a certain amount of mother liquor will be discarded sufficient to get rid of excess chloride, what fraction of the mother liquor must be thus discarded under conditions of nth operation in order to keep the percentage chloride content of the product down to one-tenth that of the soda ash?

Chloride is found in the product due to included and entrapped mother liquor, to mother liquor left adhering to the surface of the crystals and perhaps to a certain degree to solid solution. In any case, for constant crystallizing conditions, *i.e.*, constant concentration of initial solution, temperature of final solution and rate of formation of crystals, the ratio of chloride in the product to that in the mother liquor should be constant. It will, therefore, be assumed that this ratio experimentally determined in the laboratory (0.009/0.29 = 0.031) will also apply to plant conditions.

NOMENCLATURE—CONDITIONS OF nTH OPERATION

	Total weight, pounds	Weight fraction Cl	Weight fraction Na_2O
Crystals, product	C	x	u
Mother liquor	M	y	v
Soda ash	S	z	w

$1 - a$ = fraction of mother liquor discarded each time.

From the assumption above, $x = 0.1z$. An alkali balance gives

$$wS + avM = uC + vM + \text{losses}.$$

A chloride balance gives (since $y = x/0.031$)

$$zS + axM/0.031 = xC + xM/0.031.$$

It will be noted that in both balances the wash waters are ignored because the wash water from the preceding batch is identical in amount and composition with that discarded from the batch in question. An alkali balance on the laboratory data shows an output slightly greater than input. This is, of course, due to experimental inaccuracy. For plant conditions it will be assumed that fortuitous alkali losses are 1% of the daily product. Remembering that the crystallizing conditions are assumed constant and that, therefore, the value of M/C is identical with that in the laboratory experiment, 0.591, these equations can be solved, obtaining $a = 0.842$, showing that 15.8% of the mother liquor is discarded each time. The soda-ash consumption per pound of crop is 0.401. This corresponds to a soda-ash loss of 8.8%. In other words, the chemical efficiency under nth day conditions is 91.2%.

From the data tabulated above, it will be instructive to compute the volumes of solutions to be handled and of raw materials and products obtained. From these it is possible to compute the volumes of tanks and cystallizing pans required, the dimensions of storage bins necessary to hold raw materials and product for any desired time of storage, and the like.

CHAPTER IX

CRYSTALLIZATION

In approaching problems in crystallization it must be kept in mind that, where miscibility is not complete, at equilibrium any particular substance, whether gas, liquid or solid, will, at a given temperature, dissolve in a specific liquid to a definite extent. This is called its solubility in the liquid in question, and in the case of solids and liquids is usually expressed as parts by weight of the substance dissolved per 100 parts by weight of solvent. For each substance and solvent, the solubility changes with the temperature and this temperature-solubility curve must be determined experimentally. Usually, solubility shifts rapidly with the temperature, and, since the change is approximately geometric, it is best to plot the experimental points on semi-logarithmic paper. In the case of two liquids, each usually dissolves in the other; both solubilities must be determined experimentally and are normally expressed as stated above.

Each different form of the same substance has its own characteristic solubility curve, *e.g.*, the solubilities of the various allotropic forms of sulfur in benzene, etc. This is likewise true where the substance forms chemical compounds with solvent of crystallization, each such compound having its own specific solubility. Where the solubility curves of two forms intersect, the two must obviously be in equilibrium, *i.e.*, a transition point is dealt with. At any specific temperature that form having the lowest solubility is most stable; hence, on opposite sides of a transition point the stability of the two forms is interchanged.

Solvent of crystallization introduces certain confusion in expressing solubility. Although the saturated solution of a definite substance at a given temperature has a fixed composition, this may be quoted in different ways. Thus the solubility of Glauber's salt ($Na_2SO_4.10H_2O$) might be stated as the weight of this salt which, when dissolved in 100 parts by weight of water, will give a saturated solution. In this solution, however, it is impossible to distinguish between water of crystallization

and what might be called "dissolving" water. Hence the composition of this same solution might be reported as parts of anhydrous salt per 100 of total water. Furthermore, this solution might have been made up by dissolving $Na_2SO_4.7H_2O$ in water; hence, it might be convenient to have the solubility of the Glauber's salt, *i.e.*, the composition of this same solution, expressed as parts of $Na_2SO_4.7H_2O$ per 100 of water. Finally, since the anhydrous salt and that with seven waters of crystallization, as well as Glauber's salt, have their own specific solubilities, each of which, except at transition points, will differ from that of the other two salts, and since each can be expressed in terms of the other two, it is possible to have at a given temperature nine numerically different solubility figures for the system, sodium sulfate and water. However, in three groups each containing three of these solubilities, the figures are quantitatively equivalent. The following table, giving seven of these nine possible solubilities at 20°C., is taken from a standard book of chemical tables.

SOLUBILITY OF SODIUM SULPHATE AT 20°C.

Anhydrous Salt		Crystals, Decahydrate		Crystals, Heptahydrate		
Na_2SO_4	$Na_2SO_4.10H_2O$	Na_2SO_4	$Na_2SO_4.10H_2O$	Na_2SO_4	$Na_2SO_4.7H_2O$	$Na_2SO_4.10H_2O$
52.76	361.5	19.40	58.35	44.73	140.0	243.4

Computation shows that, in the last number, two of the digits are transposed. It will be instructive to compute, one from the other, the corresponding solubilities in each of the three groups.

Because of the simplification, modern tables usually give all solubilities, as parts by weight of anhydrous salt per 100 parts by weight of solvent or of solution, at the same time stating clearly the nature and the composition of the solid phase. In older tables the practice is divergent.

Under commercial conditions of crystallization, there are usually present in the form of dust sufficient nuclei so that the most stable phase separates out. Furthermore, in pan crystallization with slow cooling, equilibrium is approached closely, the difference not infrequently amounting to less than a degree, because, if crystals form at the bottom of the pan, the solution from which they deposit becomes lighter, rises to the top and is replaced by heavier, while if the crystals form initially at the

top, as soon as they get heavy enough to fall, their downward motion stirs up the whole liquid, thus keeping the composition of the solution substantially uniform in any case. Computation may, therefore, safely be based on the assumption of equilibrium.

During crystallization, in the absence of evaporation, the "dissolving" solvent, *i.e.*, that in the solution in excess of solvent of crystallization corresponding to that form of crystal which separates out, remains constant during the process and is, therefore, a suitable basis for computation. Thus, if a solution consisting of 80 g. of $Na_2SO_4.10H_2O$ dissolved in 100 g. of water be cooled to a temperature at which the solubility expressed as parts of $Na_2SO_4.10H_2O$ per 100 of water is 20, 60 g. of this salt will separate out, leaving a mother liquor of 120 g. The relations in other solutions falling between the same concentration limits are, of course, found by proportion. Where evaporation takes place it must be allowed for.

The following problems require in solution the introduction of no principles other than those already explained. Unless otherwise stated, all solubilities are given as parts by weight of anhydrous salt per 100 of solvent.

PROBLEMS

1. One thousand two hundred pounds of $Ba(NO_3)_2$ are dissolved in sufficient water to form a solution saturated at 90°C., at which temperature the solubility is 30.6. This solution is cooled without evaporation to 20°C., where the solubility is 8.6. What is the weight of water required for solution and of the crop of crystals obtained? *Ans.* 3,920 lb. water; 862 lb. crop.

2. One thousand pounds of KCl are dissolved in sufficient water to make a saturated solution at 90°C., at which temperature its solubility is 53.8. This solution is cooled without evaporation to 20°C., at which temperature its solubility is 34.7. What is the weight of water required for solution, and what is the weight of the crop of crystals obtained? *Ans.* 1,857 lb. of water, 355 lb. of crop.

3. One thousand six hundred pounds of a 16% solution of $Ba(NO_3)_2$ are cooled from 90°C. without evaporation to 20°C. (see problem 1). What crop is obtained? *Ans.* 140.7 lb.

4. One thousand pounds of a 30% solution of KCl are cooled from 90°C. without evaporation to 20°C. (see problem 2). What crop is obtained? *Ans.* 57.1 lb.

5. Solve problem 1 on the assumption that 10% more water is to be used than that necessary to give a saturated solution. *Ans.* 829 lb. crop.

6. Solve problem 2 on the assumption that $12\frac{1}{2}$% more water is to be used than that necessary to give a saturated solution. *Ans.* 2,090 lb. water, 274 lb. crop.

7. Solve problem 1 on the assumption that the solution is to be made up 90% saturated at 90°C. *Ans.* 826 lb. crop; 3,920 lb. water.

8. Solve problem 2 on the assumption that the solution is to be made up 87½% saturated at 90°C. *Ans.* 2,125 lb. of water, 263 lb. of crop.

9. Solve problems 1 and 3 on the assumption that in each case 5% of the water in the original solution will evaporate on cooling. *Ans.* 880 and 148.3 lb.

10. Solve problems 2 and 4 on the assumption that in each case 7½% of the water in the original solutions will evaporate during the cooling. *Ans.* 1,857 lb. water, 403 lb. crop; 75.2 lb. crop.

11. Solve problems 1 and 3 on the assumption that in each case, on cooling, the loss in weight of the original solution due to evaporation will be 5%. *Ans.* 885 and 147 lb.

12. Solve problems 2 and 4 on the assumption that in each case, on cooling, the loss in weight of the original solution due to evaporation will be 7½%.

CHAPTER X

MISCELLANEOUS PROBLEMS

The preceding chapters deal with problems in particular fields of industrial chemistry, developing, however, certain methods of calculation well adapted for general use. The principles underlying the calculations are in all cases the same, involving only the laws of conservation of matter and of energy and the law of combining weights. Applied chemistry is too broad to warrant, in such a book as this, separate treatment of each of its industries, but in this final chapter are given the solutions of a few problems of general interest and significance, from various sources.

Measurement of Gases by Dilution.—In a certain plant, it is desired to determine the velocity of the gas flowing through an irregularly shaped duct in which no measuring devices are installed and in which they cannot well be used. Analysis shows that the gas contains 0.24% CO_2. It is decided to determine the quantity flowing by bleeding into the gas stream CO_2 from a small, weighed cylinder. A constant rate is maintained by means of a flow meter and, after thorough mixing of the gases by passing around several bends, the average analysis of the mixture is found to be 1.41% CO_2. The loss in weight of the cylinder is 7.94 lb. in 5 min., measured by a stop watch. If the temperature of the gas is 120°F., what is its volume, in cubic feet per minute?

Solution.—The ratio of CO_2 to CO_2-free gas in the original is 0.24/99.76 = 0.0024, and the same ratio after mixing is 1.41/98.59 = 0.0143. The increase in this ratio, 0.0119, represents the mols of CO_2 bled in per mol of CO_2-free gas. Using this figure and the data given in the problem, the volume is

Pounds CO_2 per minute	Mols CO_2	Mols CO_2-free gas	Mols original gas	Cubic feet S. C.	
7.94		1	100	359	$\frac{580}{492}$ = 1,285 cu. ft. per minute.
5.00	44	0.0119	99.76		

Dilution of this sort is a method of measurement worthy of wider use. It is especially valuable for corrosive gases and liquids and in awkward mechanical situations. In using it for gases, it is important not to overlook the water vapor in the gas.

Hydrogenation and Electrolysis.—A fish oil with an iodine number of 150 is to be hydrogenated to an iodine number of 60. The hydrogen employed is produced by the electrolysis of a solution of caustic soda in a diaphragm cell. The hydrogen is then carefully washed with water to free it from entrained caustic, passed through a hot tube filled with copper gauze, cooled, dried and sent to the hydrogenator in which the efficiency of utilization of the hydrogen is approximately 90%. The hydrogen leaving the cell shrinks 1.6% when passed over phosphorus, and the oxygen leaving the anode compartment, when absorbed in pyrogallate, leaves a residue of 11%. The electrolysis is carried out at a voltage of 3.7 volts per cell, 30 cells being used in series. The power cost is 1.5 cts. per kilowatt-hour.

1. What is the hydrogen consumption in cubic feet, S. C., per 100 lb. of fish oil hydrogenated?

2. What is the power cost of this hydrogen?

3. What will be the current consumption for a hydrogenation unit with a capacity of 1,000 lb. of fish oil treated per hour?

Solution.—1. As the iodine number represents the number of centigrams of iodine added per gram of oil, this may be converted into equivalents, giving $1.5/127 = 0.0118$ equivalent per gram of original oil and $0.6/127 = 0.0047$ equivalent per gram of hydrogenated oil. In terms of hydrogen, it is seen from these figures that, even if the oil were completely hydrogenated, the weight would not change greatly. It may, therefore, with little error be assumed that these two analyses are on the same basis.[1] The hydrogen used will be $0.0118 - 0.0047 = 0.0071$ gram equivalent per gram of oil, or 0.0071 lb. equivalent (or atom) per pound of oil. The efficiency of utilization being 90%, the number of equivalents of hydrogen employed in the hydrogenator will be $(100)(0.0071)/0.90 = 0.789$ per 100 lb. of oil and the volume of this gas is $0.789/2)359 = 142$ cu. ft. at S. C.

2. Owing to diffusion, oxygen also appears in the cathode compartment, the analysis showing that the cathode gas con-

[1] If the oil were adding some other element than hydrogen, this simplification could not be made, due to the relatively large change in weight of the oil before and after addition.

tains 1.6%. On passing this gas over hot copper, all the oxygen is consumed by combustion with the hydrogen. One hundred mols of this gas, containing 1.6 mols of O_2 and 98.4 mols of H_2, will, after the removal of the oxygen, leave 95.2 mols of H_2, owing to the disappearance of 3.2 mols to form water vapor. Consequently, $0.789(98.4/95.2) = 0.815$ equivalent of hydrogen must be produced in the cathode compartment.

Diffusion also carries hydrogen over into the oxygen side to the extent of 11%. The total number of equivalents of each of these gases generated must be the same, however, *i.e.*, the mols of hydrogen must be twice the number of mols of oxygen. To get the power cost, it is necessary to know the total number of equivalents of electricity passed through the cell. Hence, the equivalents of hydrogen which have diffused to the oxygen side must be determined and added to the 0.815 equivalent calculated above. Let x represent the number of mols of hydrogen in the anode compartment. Then the total mols of hydrogen will be $x + 0.815/2$. The mols of oxygen in the anode compartment are obtained by multiplying the mols of hydrogen by the molal ratio as determined by the analysis. This equals $(89/11)x$. The mols of oxygen diffusing to the cathode side are also obtained by multiplying the mols of hydrogen produced there by the molal ratio of oxygen to hydrogen in that gas, and amount to $(0.815/2)(1.6/98.4)$. The sum of these two quantities is $8.09x + 0.0066$. Since the total hydrogen equals twice the total oxygen, $x + 0.815/2 = 2(8.09x + 0.0066)$, whence x is found to be 0.026 mol. The total hydrogen made is, therefore, $0.815 + 0.026(2) = 0.867$ equivalent.

As each gram equivalent requires 96,500 amp.-sec., each pound equivalent uses 454 times this quantity, since there are 454 g. to the pound. Thus, the power cost is

$$\frac{\text{Pound equivalents } 0.867}{} \left| \frac{\text{Ampere-seconds } (454)(96,500)}{} \right| \frac{\text{Ampere-hours}}{3,600} \left| \frac{\text{Watt-hours } 3.7}{} \right| \frac{\text{Kilowatt-hours}}{1,000} \left| \frac{1.5}{} \right. = 58.5 \text{ cts.}$$

This is figured on the basis of one cell. The fact that there are 30 cells in series would not change the result, because, although the voltage drop across the entire system would be 30 times as

great, the amperage in each cell would be only one thirtieth as much.

3. Sufficient data are now at hand to calculate the current consumption for a hydrogenation unit with a capacity of 1,000 lb. of fish oil per hour. Assume 30 cells in series as before.

Basis.—1 sec.

$$\frac{\text{Pounds oil}}{\text{3,600}} \left| \frac{\text{Equivalents of H}}{\text{100}} \right| \frac{\text{Equivalents, per cell}}{\text{30}} \left| \frac{(454)(96,500)}{\text{1,000}} \right. = 3{,}510 \text{ amp.}$$

The last step in the above calculation consists in multiplying the number of equivalents per cell per second by the number of ampere-seconds required per equivalent to get the number of amperes per cell, which, if the cells are in series, is the current consumption of the unit.

Absorption of Hydrochloric Acid.—HCl gas is absorbed from air in water in a countercurrent system of three towers, filled with coke, over which the water trickles and through which the gas rises. The gas enters the bottom of each tower and is led from its top to the bottom of the next through an unglazed earthenware pipe. The towers themselves are of dense, glazed tile, each tower in a single piece, carefully painted on the outside with multiple coats of asphalt paint. The gas is drawn through the towers by an exhauster attached to the gas discharge of the third tower, the whole system being under slight suction. The HCl solution is pumped from the bottom of each tower to the top of the next preceding one in the series. The production is 2,640 lb. per hour of 36.2% HCl, 1.18 sp. gr. The tower temperatures average 28°C.; the barometer is 29.1 in.

Liquor Analyses

Sample taken at liquor exit from each tower

	Tower 1	Tower 2	Tower 3
Per cent HCl.....	36.2	29.9	21.3

GAS ANALYSES

First three samples taken at bottom of each tower

	Tower 1	Tower 2	Tower 3	Leaving tower 3
Per cent HCl.....	43.1	26.0	19.0	0.2

1. Calculate the per cent of the total acid absorbed which is dissolved in each of the three towers.

(*a*) Using the liquor analyses only.

(*b*) Using the gas analyses only.

2. Calculate the quantity of air (HCl-free) entering both the first and second towers.

3. Calculate the volume of gas leaving the third tower per minute.

Solution. 1*a*. *Basis.*—100 lb. of entering water.

Pounds HCl leaving tower 1, (36.2/63.8)100 = 56.75

Pounds HCl leaving tower 2, (29.9/70.1)100 = 42.65

Pounds HCl leaving tower 3, (21.3/78.7)100 = 27.05

Per cent absorbed in tower 1, (100)(56.75 − 42.65)/56.75 = 24.85

Per cent absorbed in tower 2, (100)(42.65 − 27.05)/56.75 = 27.5

Per cent absorbed in tower 3, (100)(27.05)/56.75 = 47.65

1*b*. *Basis.*—100 mols HCl-free gas.

Mols HCl entering tower 1, (43.1/56.9)100 = 75.8

Mols HCl entering tower 2, (26.0/74.0)100 = 35.15

Mols HCl entering tower 3, (19.0/81.0)100 = 23.45

Mols HCl leaving tower 3, (0.2/99.8)100 = 0.2

Mols absorbed, 75.8 − 0.2 = 75.6

Per cent absorbed in tower 1, (100)(75.8 − 35.15)/75.6 = 53.8

Per cent absorbed in tower 2, (100)(35.15 − 23.45)/75.6 = 15.45

Per cent absorbed in tower 3, (100)(23.45 − 0.2)/75.6 = 30.75

If continuity of operation is assumed, the wide divergence between the per cent HCl absorbed in each of the towers, calculated from the two sets of data, must be due to one or more of the following reasons:

1. Error in the liquor or gas analyses, or both.
2. Water leaks.
3. Air leaks.

The analytical data are assumed to be reliable; if not, it is useless to attempt any further solution of the problem. The trouble is evidently not due to the second cause, since water leaks would have been noticed during the test. Gas leaks could not be detected, however, as such leaks would have been into the system because it was under suction.

2. If the discrepancy between the two sets of results is due to air leakage, the percentages absorbed as calculated from the gas analyses are in error, whereas those from the liquor analyses are accepted as representing the facts.

From these true percentages and from the gas analyses, which correctly represent the conditions at the points taken, the amounts of air, or HCl-free gas, entering each tower can be calculated. In order to do this, a basis of calculation must be chosen such that the quantities of gas can be compared on a common basis. Ordinarily, if there were no air leaks, the calculations shown under paragraph 1*b* would suffice, but because of leaks they are not on a common basis. The gas analyses on the third tower may be used, however, because that was the only one of the three on which both gas analyses were taken within the tower itself. These two analyses can safely be placed on a common basis since, owing to the tower construction, air leaks in it seem impossible. The hydrochloric acid absorbed can be made a basis for the solution of this part of the problem.

Basis.—100 mols of HCl absorbed.

From the percentages of the total acid absorbed in each of the towers as calculated from the liquor analyses, the mols absorbed in each tower will be as follows: in tower 1, 24.85 mols; in tower 2, 27.5 mols; and in tower 3, 47.65 mols. From the gas analyses on the third tower, it has already been shown that 0.2 mol was lost for every 23.25 mols absorbed in that tower. Consequently, on the above basis, the mols lost from the system are 47.65(0.2/23.25) = 0.41 mol. Thus, 100.4 mols are sent to the towers for every 100 absorbed. By using the gas analysis at the entrance of each tower, the mols of HCl-free gas at that point can be computed:

Mols HCl entering tower 1	100.4
Mols HCl-free gas entering tower 1	100.4(56.9/43.1) = 132
Mols HCl entering tower 2	100.4 − 24.85 = 75.55
Mols HCl-free gas entering tower 2	75.55(74.0/26.0) = 215
Mols HCl entering tower 3	75.55 − 27.5 = 48.05
Mols HCl-free gas entering tower 3	48.05(81.0/19.0) = 205

Inspection of these figures shows that the HCl-free gas entering tower 2 is within 5% of that entering tower 3. The difference must be due to lack of precision of the data, since the suction on the towers makes a decrease impossible. On the other hand, the HCl-free gas entering tower 1 is 40% less. This clearly indicates an air leak between towers 1 and 2. Taking the average of the values for the last two towers, *i.e.*, 210 mols, the air leak in the unglazed pipe carrying the gases from tower 1 to tower 2 is 210 $-132 = 78$ mols.

All of these molal quantities can, if desired, be converted into cubic feet of gas.

3. The gas leaving the third tower will be saturated with water, the vapor pressure of which at 28°C. is 1.1 in. Hg.

Pounds liquor produced	Pounds HCl absorbed	Mols HCl	Mols dry gas leaving tower 3	Cubic feet, S. C.	Cubic feet at 29.1 in.		
2,640	0.362		(205 + 0.4)	359	29.9	301	
60		36.5	100		(29.1 − 1.1)	273	= 378 cu. ft.

Recovery of Solvents.—A fabric which has been impregnated with a rubber cement having C_6H_6 as a solvent is dried at atmospheric pressure by passing flue gas over it and supplying heat in the drier to evaporate the solvent. The gas leaving the drier contains 20% of benzene by volume on a dry basis. It then passes to a cooler, where it is brought to 70°F., and the condensate removed. The gas is then returned to the drier. There is a certain amount of air leakage into the drier, however, and to compensate for this a small amount of the gas leaving the cooler is discharged to the atmosphere, while a corresponding amount of fresh flue gas is admitted to the system at a point just before the recycled gas enters the drier. The analysis of the make-up flue gas is 16.2% CO_2, 2.3% CO and 0.8% O_2. This gas is cooled and washed and enters the system at 70°F., saturated with water vapor. The discarded gas, freed from benzol before analysis, is 14.6% CO_2, 2.1%CO, and 2.8% O_2. The gas entering the drier itself, similarly analyzed, is 14.9% CO_2, 2.1%CO and 2.4% O_2. Assume complete evaporation of benzol in the drier and no leaks other than inward. The benzol on the stock entering the drier is 1,200 lb. per hour. The barometer is 29.55 in.

1. What is the volume of gas entering the drier per minute?
2. What is the volume of make-up flue gas entering the system per minute?
3. What is the percentage recovery of the benzol entering the drier?
4. How many times does a given unit of flue gas circulate through the drier before it is discarded?

Solution.—Consider the system as a whole. The sources of input are make-up flue gas, air leakage and benzol; the output consists of recovered benzol and waste gas. To find the relation between flue gas, air leak and waste gas, an oxygen balance will be used.

Basis.—100 mols of dry make-up flue gas.

This contains 0.8 mol O_2. Let x equal the mols of dry air leaking in, whence $100 + x$ will be the mols of dry, benzol-free waste gas, carrying 2.8% O_2. Therefore, the oxygen balance is

$$0.8 + (0.21)x = (0.028)(100 + x), \text{ whence}$$
$$x = 11.0 \text{ mols air and}$$
$$100 + x = 111 \text{ mols dry benzol-free waste gas.}$$

The flue gas was saturated with water vapor at 70°F., its vapor pressure at that temperature being 0.75 in. Hg. The air also contains some water vapor, but since its amount is small compared with that of the flue gas, no serious error will be introduced by assuming it too saturated. The vapor pressure of benzene at 70°F. is 3.12 in. Hg, so that its partial pressure in the gas leaving the cooler must have that value. Therefore, the benzene in the waste gas can be determined.

$$\frac{\text{Mols dry gas}}{111} \left| \frac{\text{Mols wet gas}}{29.55} \right| \frac{3.12}{(29.55 - 0.75) \mid (29.55 - 3.12)} = 13.42 \text{ mols benzene lost}$$

Consider the point where flue gas mixes with recycled gas to produce the gas entering the drier with 2.4% O_2. Assuming no air leakage in this part of the system, the amount of dry, benzol-free recycled gas, y, may be figured from another oxygen balance,

O_2 in flue gas + O_2 in recycled gas = O_2 in gas entering drier.

$$0.8 + (0.028)y = (0.024)(100 + y), \text{ whence}$$
$$y = 400.$$

The precision of the value of y calculated in this manner is very poor, because of the probable inaccuracies in the determinations of these small amounts of oxygen. See Fig. 13.

Since there is 20% of benzol in the gas leaving the drier (on the dry basis), it follows that there are 25 parts of benzol per 100 parts of dry gas at this point. Since the weight of benzol evaporated in the drier is known, the amount of gas leaving the drier could be computed if the amount of benzol in the gas entering it were known. The problem is complicated, however, by the fact that, although the benzol content of the recycled gas is known, this gas is diluted both by make-up flue gas and

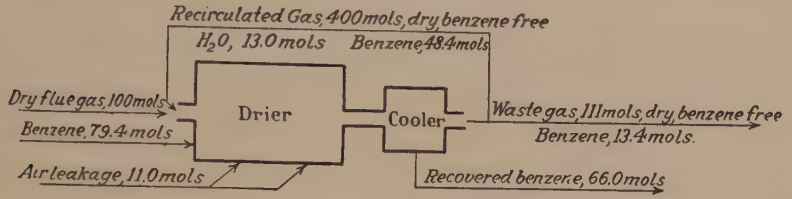


FIG. 13.—Solvent recovery problem. *Basis.*—100 mols fresh dry flue gas.

by air leaking into the drier. It is, therefore, necessary to correct the benzol content of the cycled gas for these two diluents.

Since the partial pressure of benzol in the cycled gas is 3.12 in., the partial pressure of the remaining gas must be the barometer minus this figure, or 26.43 in. However, this remaining gas contains water, in the ratio of 0.75 to 29.55. Therefore, the partial pressure of water vapor in the cycled gas is this ratio times 26.43, *i.e.*, 0.67 in. Hence, the partial pressure of dry gas is 25.77 in. Consequently, the mols of benzol per 100 mols of dry cycled gas is $100(3.12/25.77) = 12.1$. However, there are 400 volumes of this cycled gas entering the drier for each 100 of make-up flue gas, and on the same basis 11 volumes of air leaking in, making a total of 511 volumes. The 400 volumes of cycled gas carry $4(12.1) = 48.4$ mols of benzol. On the same basis, the benzol carried by the gas leaving the drier is $25(5.11) = 127.8$ mols per 100 mols of fresh dry flue gas used. Therefore, the benzol picked up in the drier is the difference in these quantities, 79.4 mols.

It has already been pointed out that the amount of cycled gas, 400 mols per 100 mols of make-up flue gas, is not a figure accurately known. It might, therefore, at first appear that the

recycled benzol, per 100 mols of dry gas used to carry it out of the drier, *i.e.*, 48.4/5.11 = 9.45, is subject to the same error. This is not the case, because most of the gas entering the drier is cycled gas saturated with benzol and the dilution of this gas by flue gas and air is, after all, only a minor correction term. Thus, if it is assumed that the ratio of cycled gas to make-up flue gas were 5:1 instead of 4:1, *i.e.*, assuming an error in this quantity of 25%, the amount of benzol entering with the cycled gas per 100 of dry gas leaving the drier, figured as above, is 9.90 instead of 9.45 mols, *i.e.*, an error of less than 5%.[1]

With these preliminary calculations, it is now possible to answer the questions in the problem.

1. The volume of gas entering the drier per minute, exclusive of air leakage, is made up of fresh flue gas and recirculated gas containing benzene, both containing water vapor. These may be tabulated as follows:

	Mols
Dry flue gas	100
Dry benzol-free recycled gas	400
Moisture with above, 500(0.75)/28.8) =	13
Recycled benzene vapor	48.4
Total gas	561.4

Basis.—1 min.

Pounds benzene	Mols benzene	Mols gas	Cubic feet, S. C.	Cubic feet at 29.55 in.		
1,200		561.4	359	29.9	530	
60	78	79.4		29.55	492	= 710 cu. ft.

[1] It takes a relatively large amount of gas to carry the benzol out of this drier. Where this gas comes from, whether flue gas or cycled gas or even air, is, from this point of view, relatively unimportant. The case is analogous to that of the tunnel kiln discussed in Chap. VI. In that case a large amount of gas was required to carry the heat forward in the kiln to the point required. Whether this gas was preheated in the cooling end of the furnace or came in as excess cold air in the combustion zone was relatively unimportant, provided heating of the stock only was being considered, but from the point of view of thermal efficiency, it was extremely desirable that the quantity of theoretical flue gas employed was made as low as possible. Similarly here, the use of make-up flue gas, while perfectly satisfactory from the point of view of drying, cuts down the efficiency of recovery of the benzol.

2. Volume of make-up gas.

Basis.—1 min.

Pounds benzene	Mols benzene	Mols dry flue gas	Cubic feet, S. C.	Cubic feet at 28.8 in.	
1,200		100	359	29.9	530
60	78	79.4		28.8	492

= 129.5 cu. ft.

3. Percentage recovery of benzol.

Basis.—100 mols of dry make-up flue gas.

$$(100)(79.4 - 13.42)/79.4 = 83.1\%.$$

4. Number of times a given unit of flue gas circulates through the drier before being discarded.

Basis.—100 mols dry make-up flue gas.

Besides this fresh flue gas, there are 400 mols of recycled gas, a total of 500 mols in process other than air leakage. Thus, the fresh flue gas makes up one-fifth of this total and may be considered as passing through the drier five times before being thrown away.

Absorption of CO_2 in Carbonate-bicarbonate Mixtures, in the Manufacture of Liquid CO_2.—By passing a clean purified flue gas up through an absorption tower fed with a so-called lye solution, made up originally with Na_2CO_3, the CO_2 content of the gas is reduced from 15.5 to 10.1%. The lye solution at entrance and exit is analyzed with 0.4844 normal HCl, using in each case 10 cc. samples of lye. For the incoming lye 13.46 cc. of acid are required to decolorize phenolphthalein and a total of 38.42 cc. to get an end point with methyl orange. For the exit liquor these values are 8.74 and 38.59 cc. respectively. One hundred ninety gallons of lye per hour are supplied to the tower, which operates at a subtantially constant temperature of 140°F.

1. What per cent of the alkali in the two solutions is in the form of bicarbonate?

2. How many pounds of CO_2 are absorbed per hour?

3. What is the volume in cubic feet per minute of the gas entering the tower?

Solution. 1. *Basis.*—10 cc. of entering liquor.

Total milliequivalents of alkali

$$(38.42)(0.4844) = 18.61.$$

Milliequivalents as bicarbonate

$$(38.42 - 2 \times 13.46)(0.4844) = 5.57.$$

Per cent in form of bicarbonate

$$(5.57/18.61)100 = 29.95\%.$$

Basis.—10 cc. of exit liquor.

Total milliequivalents of alkali

$$(38.59)(0.4844) = 18.68.$$

Milliequivalents as bicarbonate

$$(38.59 - 2 \times 8.74)(0.4844) = 10.22.$$

Per cent in form of bicarbonate

$$(10.22/18.68)100 = 54.75\%.$$

2. Since these results are based on the alkali present, they are directly comparable. Hence, the increase in the percentage conversion to bicarbonate is $54.75 - 29.95 = 24.80\%$; in other words, 24.80 equivalents of CO_2 have been absorbed per 100 equivalents of alkali used. To convert the analytical data from metric units into corresponding plant data in English units, it should be kept in mind that the ratio gram equivalents per gram is numerically identical with the ratio pound equivalents per pound. Call the specific gravity S.

Basis.—1 hr.

Gallons liquor	Pounds liquor	Equivalents of alkali	Equivalents of CO_2	
190	$8.33\,S$	0.01861	24.80	22
		$10\,S$	100	

$$= 16.1 \text{ lb. } CO_2.$$

It will be noted that the gravities cancel.

3. *Basis.*—1 min.

Pounds CO_2	Mols CO_2	Mols gas	Cubic feet, S. C.	
16.1		100	359	600
60	44	15.5		492

$$= 17.2 \text{ cu. ft. dry gas}$$

Water-gas Carburetion.—The Gas Investigation Committee of the British Institution of Gas Engineers[1] reports a careful test on a water-gas set in which the oil used showed by ultimate analysis 85.7% C, 12.7% H and 0.5% S. The rest, 1.1%, may be assumed O. They found that the tar and emulsions removed contained 20.5% of all the C in the oil used, and the analyses of the dry tars averaged 91.2% C, 6.2% H and 1.2% S, leaving 1.4% O by difference. The blue gas was 6.1% CO_2, 0.1% O_2, 38.3% CO, 50.9% H_2, 0.5% CH_4 and 4.1% N_2. The carbureted water

[1] *Gas J.*, **158**, 815 (1922).

gas was 5.2% CO_2, 5.8% illuminants, 0.1% O_2, 34.9% CO, 38.1% H_2, 10.3% CH_4 and 5.6% N_2. From these data, compute the pounds of carbon per 1,000 cu. ft. of the final product which comes from the oil and the volume of blue gas used (volumes at standard conditions, which, in the British gas industry correspond to a pound-molecular volume of 385.5 cu. ft.).

Solution.—On a basis of 100 lb. of oil, the C in the tar was 0.205 (85.7) = 17.57 lb. With this was 17.57 (6.2/91.2) = 1.19 lb. of H, 0.23 lb. of sulfur and 0.27 lb. of O. The difference, *i.e.*, oil gasified in one way or another, is 68.13 lb. of C (5.68 atoms), 11.51 lb. of H_2 (5.71 mols), 0.27 lb. of S (0.01 atom) and 0.83 lb. of O (0.05 atom). Neglecting sulfur, the net H_2 is 5.66 mols. Hence, it appears safe to assume that carbon and net hydrogen go into the gas from the oil in the ratio of 5.68 C: 5.66 H_2.

Basis.—100 mols blue gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	6.1	6.1	12.2	
O_2	0.1	....	0.2	
CO	38.3	38.3	38.3	
H_2	50.9	....	....	50.9
CH_4	0.5	0.5	....	1.0
N_2	4.1			
Total	100.0	44.9	50.7	51.9
O ≏ N_2 =			2.2	
O ≏ steam decomposed			48.5	48.5
Net H_2 =			....	3.4

Basis.—100 mols carbureted gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	5.2	5.2	10.4	
C_3H_6	5.8	17.4	....	17.4
O_2	0.1	....	0.2	
CO	34.9	34.9	34.9	
H_2	38.1	....	....	38.1
CH_4	10.3	10.3	....	20.6
N_2	5.6			
Total	100.0	67.8	45.5	76.1
O ≏ N_2 =			3.0	
O ≏ steam decomposed =			42.5	42.5
Net H_2 =			....	33.6

Call x the mols of blue gas and y the atoms of carbon in the product from the oil per mol of carbureted water gas. Set up (1) a carbon balance and (2) a *net* hydrogen balance, in each case equating the amount of the element in the blue gas plus that coming from the oil to that in the carbureted water gas.

$$0.449x + y = 0.678 \quad (1)$$
$$0.034x + (5.66/5.68)y = 0.336 \quad (2)$$
$$y = 0.309 \text{ atom C} = 3.71 \text{ lb. C}$$
$$x = 0.822 \text{ mol blue gas.}$$

This, however, is for 385.5 cu. ft. Hence, for 1,000 cu. ft. the carbon from the oil is 3.71(1,000/385.5) = 9.61 lb. Similarly, the blue gas consumption is 822 cu. ft. per 1,000 cu. ft. of product.

By entirely different measurements and methods the committee found 9.38 lb. of C and 840 cu. ft. of blue gas.

This test was conducted at a carburetor temperature of about 1330°F. This is lower than the practice in many American plants. With higher temperatures, tar formation is less. Above 1400°F. it is probably not far in error to assume as a first approximation that 90% of the C and 95% of the net H of the oil go into the gas. Of the remainder, however, some does not show up as tar but is burnt out during the air blow.

A committee report of the American Gas Association[1] gives the following data: Blue gas, 5.0% CO_2, 0.3% O_2, 38.9% CO, 51.6% H_2, 2.5% CH_4 and 1.7% N_2; finished gas, 4.1% CO_2, 10.1% illuminants, 1.0% O_2, 28.5% CO, 31.9% H_2, 14.7% CH_4 and 9.7% N_2. While they do not give the ultimate analysis of the oil, it was a Mid-continent stock of a gravity such that it probably contained very nearly 6 lb. of carbon and 0.86 lb. of net hydrogen per gallon. From these data and the assumption of the preceding paragraph compute:

1. Gallons of oil used per 1,000 cu. ft. finished gas.
2. Cubic feet of blue gas per 1,000 cu. ft. finished gas.
3. Per cent of carbon present as oxides in the finished gas which entered as oxides in the blue gas.

Solution.—The carbon entering the product from the oil is assumed to be 90% of 6 lb. = 5.4 lb. = 0.45 atom C and the hydrogen, 95% of 0.86 lb. = 0.817 lb. = 0.405 mol H_2.

[1] *Proc.* Am. Gas Assoc., 1923, 1038.

Basis.—100 mols blue gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	5.0	5.0	10.0	
O_2	0.3	....	0.6	
CO	38.9	38.9	38.9	
H_2	51.6	....	....	51.6
CH_4	2.5	2.5	....	5.0
N_2	1.7			
Total	100.0	46.4	49.5	56.6
O $\Rightarrow$ N_2 =			0.9	
O $\Rightarrow$ steam decomposed =			48.6	48.6
Net H_2 =			....	8.0

Basis.—100 mols finished gas.

	Mols	Atoms C	Atoms O	Mols H_2
CO_2	4.1	4.1	8.2	
C_3H_6	10.1	30.3	....	30.3
O_2	1.0	....	2.0	
CO	28.5	28.5	28.5	
H_2	31.9	....	....	31.9
CH_4	14.7	14.7	....	29.4
N_2	9.7			
Total	100.0	77.6	38.7	91.6
O $\Rightarrow$ N_2 =			5.15	
O $\Rightarrow$ steam decomposed =			33.55	33.55
Net H_2 =			.....	58.05

On the same basis:

x = mols blue gas.

y = gallons of oil.

Carbon balance: $0.464x + 0.45y = 0.776$

Net H_2 balance: $0.08x + 0.405y = 0.5805$

$x = 0.353$, $y = 1.36$.

Since, in American practice, the pound-molecular volume is 380 cu. ft., the oil per 1,000 cu. ft. of product is 1.36(1,000/380) = 3.58 gal. The direct measurements of the committee showed 3.69 gal., a difference of 3%. The blue gas per 1,000 cu. ft. of product is obviously 353 cu. ft. This blue gas contained 5.0 + 38.9 = 43.9% of carbon oxides = 155 cu. ft. per 1,000 cu. ft.

of finished gas. Since the finished gas contained 4.1 + 28.5 = 32.6% = 326 cu. ft. of oxides of carbon per 1,000 of product, only 100(155/326) = 47.5% of these entered as blue gas. The rest were formed in the carburetor or superheater by reaction of the excess steam from the generator. The steam probably interacts directly with hydrocarbons, but stoichiometrically the process can be considered as water-gas formation with carbon deposited by cracking. This phenomenon is much more marked in this case than in the previous one, due to the higher temperature and the correspondingly higher reaction rate. This decomposition of steam during carburetion is a decided factor in lessening tar formation.

If, in using this method, net hydrogen in the coke could be neglected, or if, as is frequently allowable, it is possible to assume the value of the ratio of net H_2:C in the generator fuel as consumed during the steam blow, it is not necessary to analyze the blue gas, but the ratio of carbon from blue gas to carbon from oil can be computed, using only the analysis of the finished gas and of the oil corrected for tar. Were there no net hydrogen in the coke, all net hydrogen in the product would come from oil alone; hence, this would be computed accurately from a net hydrogen balance. The net hydrogen in the generator fuel is only a minor correction, and hence, the computed oil value is quite dependable. The quantity of blue gas is computed from a carbon balance by difference, and is a much less accurate figure.

TABLE OF CONSTANTS

	English units	Metric units
One atmosphere	29.92 in. of Hg; 14.7 lb. per square inch	760 mm. of Hg
Standard conditions (S.C.)	32°F., 1 atm.; 492°R., 1 atm.	0°C., 1 atm.; 273°K., 1 atm.
Molecular volume, S.C.	359 cu. ft. per pound mol	22.4 l. per gram mol
Density of water (approximate)	62.4 lb. per cubic foot	1 g. per cubic centimeter
Specific gravity of mercury	13.6	13.6
One gallon of water	8.33 lb. per cubic foot	
Gas constant	1,543 in engineering units[1]	0.08207 l.-atm.
One faraday	.....	96,500 coulombs

CONVERSION FACTORS

Degrees Fahrenheit = 1.8 (°C.) + 32
Degrees Centigrade = (°F. − 32)/1.8
Degrees Rankine = °F. + 460
Degrees Kelvin = °C. + 273

1 inch = 2.540 cm.
1 foot = 0.3048 meter
1 pound (avoirdupois) = 453.6 g.

VAPOR PRESSURE OF WATER

English units		Metric units	
Temperature, degrees Fahrenheit	Pressure, inches of Hg	Temperature, degrees Centigrade	Pressure, millimeters of Hg
32	0.18	0	4.57
40	0.25	5	6.51
50	0.36	10	9.14
60	0.52	15	12.67
65	0.62	20	17.36
70	0.74	22	19.63
75	0.87	24	22.15
80	1.03	26	24.96
85	1.21	28	28.06
90	1.42	30	31.51
95	1.66	35	41.78
100	1.93	40	54.87
105	2.24	45	71.36
110	2.59	50	91.98

[1] Pressures in pounds per square foot, volumes in cubic feet, temperatures in degrees Rankine, quantities in pounds mols.

INTERNATIONAL ATOMIC WEIGHTS, 1925

	Symbol	Atomic weight
Aluminum	Al	26.97
Barium	Ba	137.37
Boron	B	10.82
Bromine	Br	79.916
Calcium	Ca	40.07
Carbon	C	12.000
Chlorine	Cl	35.457
Copper	Cu	63.57
Fluorine	F	19.00
Hydrogen	H	1.008
Iodine	I	126.932
Iron	Fe	55.84
Lead	Pb	207.20
Lithium	Li	6.940
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.61
Nickel	Ni	58.69
Nitrogen	N	14.008
Oxygen	O	16.000
Phosphorus	P	31.027
Potassium	K	39.096
Silicon	Si	28.06
Silver	Ag	107.880
Sodium	Na	22.997
Sulfur	S	32.064
Tin	Sn	118.70
Zinc	Zn	65.38

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